INDUSTRIAL OIL AND FAT PRODUCTS

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PREFACE

This volume is intended to be primarily a text on oil and fat technology, hence the greater part (comprising Sections C and D) is devoted to a description and discussion of the commercially important oil and fat products and the processes used in the manufacture of these products In two preliminary sections (A and B), the chemical and physical nature of fats and oils is briefly reviewed, and the various fatty raw materials are considered with respect to their composition, characteristics, and availability

The rapid advance of oil and fat technology in the past few years has made it possible to include much important material not available in older books All material, both old and new, has been treated critically, and the endeavour throughout has been to devote space to individual subjects in approximate proportion to their actual or potential importance to industry

Although the present text has naturally been based upon the previous literature, attention should be called to the considerable amount of technical material which is published here for the first time An attempt has been made to fill, at least partially, some of the more notable gaps in the literature of oil and fat technology These gaps occur principally in the field of edible fats and oils where there is a particular dearth of published information on plastic shortening agents and bakery products, and on the practical operations of refining, bleaching, deodorization, and hydrogenation In attempting to fill these gaps the author has had recourse to his own experience, and to the advice of many friends in the industry

In the preparation of the manuscript the author has been most fortunate in having the assistance of a number of persons who have read the individual chapters and given him the benefit of their expert advice and suggestions For their invaluable help in this particular he is deeply indebted to Robert M Walsh, G S Jamieson, K S Markley, George W Irving, Jr, S T Bauer, F G Dollear, Bruce Miller, Ralph Potts, Joe Kirby, A A Robinson, George Carlin, H P Trevithick, A S Richardson, J J Vollertsen, L E Osmer, Henry A Gardner, G G Sward, Francis Scofield, L B Parsons, Warren H Goss, and Arthur J Lewis Sincere thanks are also expressed to Mr R O Feuge, who prepared most of the original drawings for the illustrations, to Mr C H Billett for assistance in preparing photographs for many of the illustrations, to Miss Dorothy Beckemeyer for checking the literature references, to Mr Robert H McKinney for the loan of photographs for the chapter on bakery products, to the

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A E BAILEY

New Orleans Louisiana
May 16 1944

CONTENTS

A. THE NATURE OF FATS AND OILS

THE NATURE OF FATS AND OILS:

INTRODUCTION

This book proposes to describe the various fatty products of commerce and the processes by which these products are derived from crude fats and oils. It is not intended to present a comprehensive or generalized treatment of oil and fat chemistry. Since, however, it is scarcely practicable to enter upon a discussion of industrial oil and fat products without some preliminary consideration of the nature of oils and fats in general, the following section, comprising the first part of the book, will be devoted to a brief outline of the composition and the chemical and physical behavior of these materials.

Before proceeding further, an explanation is in order concerning the use of the terms "oil" and "fat." Ordinarily, a product which is liquid at ordinary temperatures is referred to as an oil, whereas one which is solid or semisolid under the same conditions is designated as a fat. Unfortunately the term "oil" is also applied to various nonfatty materials, such as essential oils and petroleum products. In order to avoid confusion in terminology, some writers have adopted the practice of using the term "fat" exclusively in speaking of both fats and oils. This simplification of the terminology unquestionably has its advantages, but it does not appear suitable for a treatise on industrial products because for these the distinction between liquid and solid materials is often important.

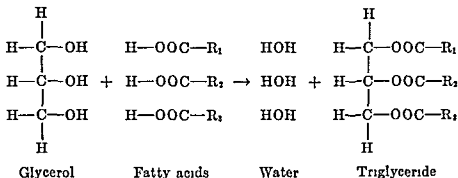
In the following pages, the terms "fat" and "oil" are used in their popular sense and, to some extent, more or less interchangeably. It is to be recognized that often no sharp distinction can be made between the two. At sufficiently low temperatures all oils will solidify, and at even moderately elevated temperatures all fats will become liquid. Furthermore, a fat is never completely solid, except under unusual circumstances. At ordinary temperatures, most fats are plastic solids, consisting of a relatively small proportion of crystalline particles, intimately mixed with liquid oil.

CHAPTER I

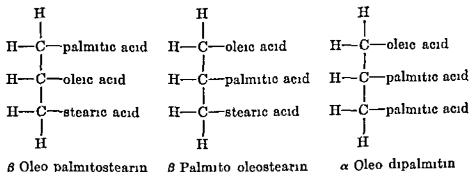
THE STRUCTURE AND COMPOSITION OF FATS AND OILS

1. The Glycerides

Oils and fats[1] may be defined as those substances of plant or animal origin which consist predominantly of triglyceryl esters of the fatty acids, or *triglycerides* From the structural standpoint, a triglyceride may be considered to be formed by the condensation of one molecule of glycerol with three molecules of fatty acids to yield three molecules of water and one molecule of a triglyceride



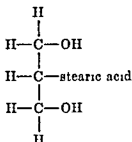
If the three fatty acids are identical, the product is a *simple triglyceride*, if they are different, it is a *mixed triglyceride* Each mixed triglyceride containing three different acid radicals has three different isomeric forms, according to which fatty acid is in the inside (β) position in the molecule, and which acids are consequently in the outside (α and α') positions Each mixed triglyceride containing two different fatty acids similarly has two isomeric forms.



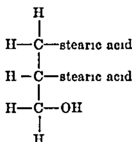
β Oleo palmitostearin β Palmito oleostearin α Oleo dipalmitin

[1] General Treatment T P Hilditch *The Chemical Constitution of Natural Fats*, Wiley, New York, 1941 J A Lovern *The Composition of the Depot Fats of Aquatic Animals*, Dept Sci Ind Res , Food Investigation Special Rept No 51 H M Stationery Office, London, 1942 H E Longenecker, *Chem Revs* , 29, 201–224 (1941)

Monoglycerides and *diglycerides* contain but one and two fatty acid radicals, respectively, and consequently have free hydroxyl groups They occur naturally only in fats which have become partially hydrolyzed, but are easily prepared synthetically and have important industrial uses



β Monostearin



α,β Distearin

The characteristics of glycerides are determined by their composition in terms of component fatty acids In considering the fatty acid composition of a glyceride it is particularly important to distinguish between the saturated acids, which are relatively high melting and unreactive, and the unsaturated acids, which have low melting points and are reactive toward oxygen and other substances

The waxes, which consist of fatty acids esterified with fatty alcohols of high molecular weight, will not be treated in this volume

Structure of Natural Glycerides

The glycerides of fats are in general highly mixed Simple trigylcerides appear to be the exception rather than the rule, they occur for the most part in the relatively few fats which contain a single fatty acid in such preponderant amount that the formation of this class of glycerides is unavoidable

A large part of our present knowledge of glyceride structure is derived from an extensive series of investigations on many different fats and oils carried out over a period of years by Hilditch and co-workers [1] These investigations have led to the deduction of a "rule of even distribution" governing the composition of natural fats According to this rule, each of the individual fatty acids of a fat tends to be apportioned as evenly as is possible among the different glyceride molecules Consequently, fatty acids which are present in minor quantities are inclined to appear but singly in the glycerides Acids which comprise more than one-third of the total fatty acids will generally appear in nearly all the glyceride molecules, and an acid must be present to the extent of at least two-thirds of the total fatty acids to form any considerable amount of simple glycerides

The fats which appear to follow most closely the principle of even distribution are those derived from vegetable seeds Vegetable fruit coat

fats are inclined to deviate somewhat from the rule, and animal fats exhibit quite marked deviations The latter are notable, in particular, for a tendency to have their saturated acids closely grouped, to form considerable proportions of fully saturated glycerides Thus, for example, beef fat may contain 12% to 20% of fully saturated glycerides, even though its content of saturated acids is not greater than 50% to 60%

Although the rule of even distribution provides a valuable clue to the general composition of fats, it should be pointed out that it represents a trend only, and that it is by no means sufficiently exact to serve as a reliable basis for the calculation of the glycerides in a fat which has been analyzed in terms of its fatty acids Hilditch and Meara[2] have outlined methods for such calculations, but these are empirical, and vary according to the composition of the fat in question, rather than conforming to the principle of true even distribution A single example will suffice to indicate the utility and the shortcomings of the principle as applied without empirical modifications

The component fatty acids of a sample of cocoa butter examined by Hilditch and Stainsby[2a] were as follows

Palmitic	26 2%
Stearic	34 4%
Oleic	37 3%
Linoleic	2 1%

In the case of this particular combination of fatty acids, calculation of the glyceride composition on the basis of true even distribution is easily carried out Neither linoleic acid nor palmitic acid can be present doubly in the same glyceride molecule, but these acids will be present singly in 6 3% and 78 6% of the glyceride molecules, respectively Stearic and oleic acids will both be present in all glyceride molecules, and in addition stearic acid will be twice present in 3 2% of the molecules, and oleic acid will be present twice in 11 9% of the molecules If the fatty acids are evenly distributed, the glyceride composition of the fat must, therefore, be as follows

Stearic oleic linoleic	6 3%
Stearic oleic palmitic	78 6%
Stearic oleic oleic	11 9%
Stearic oleic stearic	3 2%

The calculated composition of the fat compares as follows with the actual composition reported by the above authors

[2] T P Hilditch and M L Meara, *J Soc Chem Ind*, **61**, 117–125T (1942)
[2a] T P Hilditch and W J Stainsby *J Soc Chem Ind* **55**, 95–101T (1936)

		Calculated	Found
Trisaturated	Palmitic palmitic stearic	—	2 5
Disaturated	Palmitic palmitic oleic and palmitic palmitic linoleic	—	6 5
	Palmitic stearic oleic and palmitic stearic linoleic	78 6	51 9
	Stearic stearic oleic and stearic stearic linoleic	3 2	18 4
Monosaturated	Palmitic ole c oleic and palmitic oleic linoleic	—	8 7
	Stearic oleic oleic and stearic oleic linoleic	18 2	12 0

It will thus be seen that the calculation predicts the preponderance of disat urated, monounsaturated glycerides and the absence or near absence of

Table 1
Glyceride Compositions of Various Fats and Oils

Fat	Fatty ac ds mole per cent		Glycer des[i] mole per cent			
	Satd	Unsatd	SSS	SSU	SUU	UUU
Cocoa butter[a]	59 8	40 2	2	77	21	—
Mutton tallow[b]	57 2	42 8	14	54–48	25–38	7–0
Palm oil[c d]	52 5	47 5	8	54	32	6
Lard[e]	50 4	49 6	9	48–43	35–45	8–3
Lard[e]	42 4	57 6	5	39–32	46–60	10–3
Cottonseed[c,f]	28 4	71 6	—	13	59	28
Peanut oil[c g]	19 2	80 8	—	1	56	43
Olive oil[c,h]	15 1	84 9	—	—	45	55

6)

en ited glyc
saturated
glycerides

trisaturated and triunsaturated glycerides but fails to indicate the dis tribution of acids within the two classes of disaturated and monosaturated glycerides

The analytical data collected in Table 1 illustrate the characteristic glyceride compositions of vegetable oils containing different proportions of saturated and unsaturated fatty acids and also show the difference between vegetable oils and animal fats of similar fatty acid composition

It should be mentioned that while the Hilditch technique provides a direct method for the estimation of completely saturated glycerides methods for the estimation of other classes of glycerides are much less

straightforward and reliable. Evidence for the absence of unsaturated simple glycerides in vegetable seed oils rests upon a particularly uncertain foundation Recent data obtained by various workers who have fractionated these oils indicate that there is a rather greater tendency for the grouping of unsaturated acids than might be inferred from the principle of even distribution Thus Riemenschneider, Swift, and Sando[3] found definite evidence of the presence of trilinolein in a fractionally crystallized fraction of cottonseed oil Goss[4] has obtained, by means of liquid-liquid extraction, 20% of oil with an iodine value of 178 from normal soybean oil Walker and Mills,[5] by means of chromatography, separated a fraction of iodine value 246 5 (hence containing trilinolenin) from a linseed oil with a linolenic acid content of 50 5% It is also noteworthy that, whereas Hilditch and Paul[6] originally concluded that the presence of triunsaturated glycerides in lard and tallows was improbable, the later and more refined work of Hilditch and Pedelty,[7] Hilditch and Zaky,[8] and Hilditch and Murti[9] has strongly suggested their presence in these fats in appreciable amounts

Jackson and Longenecker[10] have recently noted a marked tendency toward *random* rather than *even* distribution in the fatty acids of babassu oil Longenecker[11] has suggested that animal fats in general may conform to the random distribution pattern However, there are undoubtedly considerable deviations from such a pattern; experiments carried out by the author have shown that the melting points, micropenetrations, and other physical properties of hog and beef fats are considerably altered by treatment of the fats (see page 681) to produce a completely random arrangement of the fatty acids within the glyceride molecules

2. The Fatty Acids

The molecular weight of the glyceryl portion (C_3H_5) of a triglyceride molecule is 41 The combined molecular weight of the fatty acid radicals (R COO) comprising the remainder of the molecule will vary with different oils from an average of about 650 to 970 Thus the fatty acids contribute from 94% to 96% of the total weight of the molecule

[3] R W Riemenschneider, C E Swift, and C E Sando, *Oil & Soap*, **17**, 145–148 (1940)

[4] W H Goss, *private communication* (1944)

[5] F T Walker and M R Mills, *J Soc Chem Ind*, **62**, 106–109 (1943)

[6] T P Hilditch and S Paul, *Biochem J*, **32**, 1775–1784 (1938)

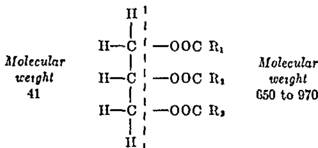
[7] T P Hilditch and W H Pedelty, *Biochem J*, **34**, 971–979 (1940)

[8] T P Hilditch and Y A H Zaky, *Biochem J*, **35**, 940–951 (1941)

[9] T P Hilditch and K S Murti, *Biochem J*, **34**, 1301–1311 (1940)

[10] F L Jackson and H E Longenecker, *Oil & Soap*, **21**, 73–75 (1944)

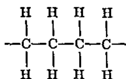
[11] H E Longenecker, *Chem Revs*, **29**, 201–224 (1941)



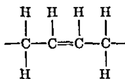
Because of their preponderant weight in the glyceride molecules, and also because they comprise the reactive portion of the molecules, the fatty acids greatly influence the character of the glycerides Consequently, the chemistry of fats and oils is to a very large extent the chemistry of their fatty acids

The naturally occurring fatty acids are in general normal, monobasic aliphatic compounds, consisting almost without exception of a single carboxyl group attached to the end of a straight hydrocarbon chain With a single exception (isovaleric acid), the fatty acids which are found in nature contain an even number of carbon atoms The individual acids differ from one another primarily in the number of carbon atoms in their chains, and the number and position of the ethylenic linkages or double bonds between the carbon atoms

Those fatty acids in which all carbon atoms are linked with not less than two hydrogen atoms, and which thus contain no double bonds, are termed *saturated* The fatty acids which contain double bonds are termed *unsaturated* The degree of unsaturation of an oil depends upon the average number of double bonds in its fatty acids



carbon chain of a saturated acid

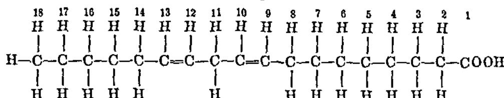


carbon chain of an unsaturated acid

The more common fatty acids are usually referred to by name, as lauric, palmitic, oleic, etc The Geneva nomenclature provides a scheme for applying to each acid a name definitive of its chemical composition Under this system, the number of carbon atoms is indicated by a Greek prefix Thus acids of 12, 14, 16, and 18 carbon atoms take the respective prefixes, dodec-, tetradec-, hexadec-, octadec-, etc Saturated acids are distinguished by the suffix, -anoic, and unsaturated acids by the suffix, -enoic Palmitic acid, for example, is designated as hexadecanoic acid

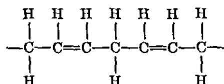
The number of double bonds in the fatty acids is indicated by a suitable

prefix, thus, linoleic acid, with two double bonds, is a dienoic acid, while linolenic acid, with three double bonds, is a trienoic acid The position of the double bonds is indicated by prefixing the numbers of the carbon atoms between which the double bonds occur In numbering the carbon atoms, the one in the carboxyl group is designated as number one, and the remainder are numbered consecutively to the end of the chain

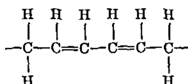


9 10, 12 13 octadecadienoic (linoleic) acid

Polyunsaturated fatty acids of the *nonconjugated* type, in which no two adjacent carbon atoms are connected to double bonds, are to be distinguished from *conjugated* acids, in which single and double bonds alternate between the carbon atoms



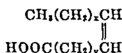
nonconjugated fatty acid chain



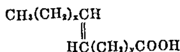
conjugated fatty acid chain

Conjugated fatty acids and their glycerides are much more reactive, *i e*, they oxidize and polymerize more readily, than the corresponding nonconjugated acids and glycerides

The unsaturated fatty acids are capable of existing in either the *cis-* or the *trans-* form, according to whether the two portions of the molecule joined by the double bond extend in the same direction or in opposite directions from their point of juncture The number of possible *cis trans*



Cis form of monoethenoid acid



Trans form of monoethenoid acid

isomers increases rapidly with an increase in the number of double bonds A monoethenoid acid may exist in two forms, *cis-* or *trans-* A diethenoid acid may exist in four forms *cis-cis-*, *cis trans* , *trans-cis-*, and *trans trans-* A triethenoid acid may exist in the form of eight different isomers, etc Apparently only the *cis-* forms exist in nature, but the *cis* may be converted to the *trans* form by certain treatments in the processing of fats and oils

The average degree of unsaturation of a fat or fatty acid, etc , is measured by its iodine value, which is defined as the percentage of iodine absorbed

by the material, on the basis of its own weight One diatomic molecule of iodine is added quantitatively at each double bond of nonconjugated fatty acid chains In the case of conjugated acid chains, the absorption of iodine is variable, according to the conditions of reaction, but is always less than that corresponding to one molecule per double bond. The average chain length or average molecular weight of a fat is indicated by its saponification value or its saponification equivalent The saponification value is the number of milligrams of potassium hydroxide required to saponify one gram of the fat The saponification equivalent is the parts by weight of fat saponified by 56 104 parts of potassium hydroxide The relation between the two is saponification value equals 56,104 divided by saponification equivalent Numerically, the saponification equivalent is equal to one-third the average molecular weight of the fat The neutralization value and the neutralization equivalent bear the same relation to the fatty acids as do the saponification value and the saponification equivalent to the glycerides The neutralization equivalent of a sample of fatty acids is numerically equal to the average molecular weight of the acids

In addition to the ordinary fatty acids described above, there are a limited number of natural fatty acids with peculiarities of structure, such as triple bonds, substituted hydroxyl or ketone groups, or closed carbon rings These acids will be discussed individually in a later section (page 20)

(a) *Saturated Fatty Acids*

The saturated fatty acids occurring in fats and oils are listed in Table 2, together with their molecular weights and certain characteristics calculated from the molecular weights The boiling points of the saturated acids, the melting points, and the melting points of the corresponding triglycerides are listed in Table 3 Other properties and characteristics of these acids will be discussed in the later chapters devoted to the reactions and physical *properties of fats and fatty acids*

The vapor pressures of the acids at a given temperature increase regularly with an increase in molecular weight The difference in boiling point between adjacent members of the series is sufficient to permit efficient separation of different saturated acids from mixtures by means of fractional distillation

The melting points of the saturated acids exhibit a progressive increase as the carbon chain is lengthened Differences in the melting points of the acids are reflected in the melting points of the simple triglycerides, as noted in Table 3, and also in those of the mixed triglycerides Thus, milk fats and vegetable fats of the coconut oil type, which contain large proportions of C_6 to C_{12} acids, are much lower in melting point than fats of an equivalent degree of unsaturation which are composed of C_{16} and C_{18} acids

Butyric and *caproic* acids are found in appreciable quantity only in milk fats, where each may occur to the amount of 2-4% by weight of the total fatty acids *Caprylic* and *capric* acids occur in milk fats and in coconut and palm kernel oils to the extent 1 to 8% each *Lauric* acid constitutes 40–50% of the total fatty acids of coconut and the various palm kernel

TABLE 2
THE NATURALLY OCCURRING SATURATED FATTY ACIDS, THEIR MOLECULAR WEIGHTS, AND CERTAIN OF THEIR CALCULATED CHARACTERISTICS

Common name	Systematic name	Number of C atoms	Molecular weight of the acid	Molecular weight of its triglyceride	Neutralization value of the acid	Saponification value of the triglyceride
Butyric	Butanoic	4	88 10	302 4	636 8	556 6
Caproic	Hexanoic	6	116 16	386 5	483 0	435 5
Caprylic	Octanoic	8	144 21	470 7	389 0	357 6
Capric	Decanoic	10	172 26	554 8	325 7	303 4
Lauric	Dodecanoic	12	200 31	639 0	280 1	263 4
Myristic	Tetradecanoic	14	228 36	723 1	245 7	232 8
Palmitic	Hexadecanoic	16	256 42	807 3	218 8	208 5
Stearic	Octadecanoic	18	284 47	891 5	197 2	188 8
Arachidic	Eicosanoic	20	312 52	975 6	179 5	172 5
Behenic	Docosanoic	22	340 57	1059 8	164 7	158 8
Lignoceric	Tetracosanoic	24	368 62	1143 9	152 2	147 1
Cerotic	Hexacosanoic	26	396 67	1228 0	141 4	137 1

TABLE 3
BOILING POINTS OF THE SATURATED FATTY ACIDS AND MELTING POINTS OF THE ACIDS AND THE CORRESPONDING SIMPLE TRIGLYCERIDES

Acid	Boiling point °C at 16 mm	Melting point of acid °C	Melting point of triglyceride °C [a]
Butyric	163 (at 760 mm)	−8	—
Caproic	107	−1	—
Caprylic	135	16	—
Capric	159	31 3	31 5
Lauric	182	43 5	46 4
Myristic	202	54 4	57 0
Palmitic	222	62 9	65 5
Stearic	240	69 6	71 5
Arachidic	—	75 4	—
Behenic	—	80 0	—
Lignoceric	—	84 2	—

[a] Melting point of the highest melting, most stable crystal modification

oils, and is found in small amounts, *i e*, 2-6%, in milk fats *Myristic* acid is a minor constituent (2% or less) of many common seed oils, fruit coat oils, and animal fats It occurs in milk fats to the extent of 8–12%, and in coconut and palm kernel oils to the extent of 15–30% It is a major component of seed fats of the *Myristicaceae* family (nutmeg butter, ucuhuba butter, etc), where it may constitute 70–80% of the total fatty acids

Palmitic acid is the most widely distributed of the saturated fatty acids It occurs in practically all animal and vegetable fats to the extent of at least 6 8%, and is a major constituent of lard, tallow, palm oil and cocoa butter *Stearic* acid is also widely distributed Most vegetable oils contain in the neighborhood of 1–3% Lard, tallow, and cocoa butter contain approximately 8%, 17%, and 35%, respectively *Arachidic, behenic,* and *lignoceric* acids do not occur in quantity in any fat or oil, although milk fats and many seed oils contain these acids in small amounts The richest source of these acids of higher molecular weight is peanut oil, which contains from 1–3% of each

(*b*) *Unsaturated Fatty Acids*

The unsaturated acids which occur in fats and oils are known with much less certainty than the saturated acids because of the relative difficulty of isolating and characterizing these compounds The highly unsaturated fatty acids of four or more double bonds, which are found principally in marine oils, are particularly difficult subjects for study, because of the readiness with which they isomerize or polymerize under the influence of heat or chemical reagents At the present time, therefore, the naturally occurring fatty acids present a somewhat ill-defined picture In general, those of a limited degree of unsaturation may be said to have been more or less clearly identified, but much confusion and uncertainty exists concerning the more unsaturated members

In the following section, the individual unsaturated acids will be mentioned first in the order of their degree of unsaturation, and second in ascending order of their molecular weights Discussion will be confined to the ordinary acids containing straight hydrocarbon chains, the relatively few unsaturated acids of abnormal structure will be considered later (page 20), as will acids which are not found in nature, but may be prepared synthetically, or produced by processing treatments commonly applied to natural oils or their fatty acids (page 21)

A decenoic acid (10 carbon atoms with 1 double bond) has been found in traces in butter fat [12] Its double bond is in the 9 10 position Another, 4 5, decenoic acid is said to occur in small quantities in a few commercially unimportant seed fats [13]

Traces of 9 10 dodecenoic or *lauroleic* acid (12 C atoms, 1 double bond) have been reported in butterfat [14] and the corresponding 4 5 acid occurs in the seed fats mentioned in the preceding paragraph There are traces of a dodecenoic acid of uncertain configuration in sperm whale and porpoise

[12] A W Bosworth and J B Brown *J Biol Chem* **103**, 115–134 (1933)

[13] Y Toyama *J Soc Chem Ind Japan* **40**, 285–289B (1937) S Komori and S Ueno *Bull Chem Soc Japan* **12**, 433–435 (1937)

[14] T P Hilditch and H E Longenecker, *J Biol Chem*, **122**, 497–506 (1937)

oils[15] The head oil of the sperm whale contains 4% of a dodecenoic acid of undetermined configuration[16]

Butterfat contains in the neighborhood of 1% of 9 10 tetradecenoic or *myristoleic* acid (14 C atoms, 1 double bond)[12] Small amounts of the 4 5 acid occur in the seed fats mentioned above The 9 10 acid is found in traces in most marine oils, and a 5 6 dodecenoic acid is found in considerable quantity in sperm whale head oil,[16, 17] and in the blubber fat of the sperm whale and other toothed whales[1, 15] There are probably traces of tetradecenoic acid in many land animal fats

Palmitoleic, 9.10 hexadecenoic acid (16 C atoms, 1 double bond) is present in traces, *i e*, about 1% or less, in many vegetable oils, including olive, palm, cottonseed, peanut, and soybean oils It is present in milk fats, and in lard, tallow, etc , in slightly greater amounts, (*e g*, 2-3%), and is found in the fats of birds, reptiles and amphibia in still greater quantity (6–15%) In the fats of most whales and fishes, including those from which whale and fish oils are obtained commercially, palmitoleic acid comprises from 10 to 20% of the total fatty acids Hilditch[1] has pointed out that, in animal fats, there is a progressive decrease in the proportion of this acid corresponding to the evolutionary development of the animal Only the 9 10 form of hexadecenoic acid has thus far been reported in nature

Oleic acid, 9 10 octadecenoic acid (18 C atoms, 1 double bond), is the most widely distributed of all fatty acids It occurs in some quantity in all fats and oils In most liquid vegetable oils it is a major component, accounting for 20% or more of the total fatty acids, and *in many important* oils, including olive oil, palm oil, peanut oil, sesame oil, corn oil, and sunflowerseed oil, it is the principal acid In milk fats, lard, and tallows it is also the chief acid, and it occurs in considerable quantity in virtually all animal fats whether of land or marine origin It is a minor component only of the highly saturated lauric acid oils and a few other oils, such as castor oil and tung oil, which consist predominantly of a single glyceride

Two other natural octadecenoic acids appear to have been *positively identified* These are *petroselenic* acid, which contains a double bond in the 6 7 position, and vaccenic acid, in which this bond is in the 11 12 position Petroselenic acid is peculiar to parsley seed oil and other commercially unimportant seed oils of the *Umbelliferae* and *Araliaceae*, in which it is a major component *Vaccenic* acid occurs in traces in beef fat and possibly in other animal fats and butterfat[18, 19]

[15] Y Toyama and T Tsuchiya, *Bull Chem Soc Japan*, 10, 563–570 (1935)
[16] T P Hilditch and J A Lovern, *J Soc Chem Ind*, 47, 105–111T (1928)
[17] M Tsujimoto, *J Soc Chem Ind Japan*, 30, 10 (1927)
[18] J Grossfeld and A Simmer, *Z Untersuch Lebensm*, 59, 237 258 (1930)
[19] S H Bertram, *Biochem Z*, 197, 433–441 (1928)

Millican and Brown[19a] have reported experimental results which suggest the presence of octadecenoic acids other than ordinary oleic acid not only in many animal fats, but also in soybean and rapeseed oils

Gadoleic acid,[20, 21] 9:10 eicosenoic acid (20 C atoms, 1 double bond) is a minor component of many, if not virtually all marine oils Eicosenoic acids apparently do not occur in vegetable oils or in land animal fats

Erucic acid, 13:14 docosenoic acid (22 C atoms, 1 double bond), is found only in oil from seeds of the *Cruciferae* It comprises in the neighborhood of 50% of the total fatty acids of both rapeseed and mustardseed oil *Cetoleic* acid,[22] 11.12 docosenoic acid, like gadoleic acid, is a minor component of many marine oils

Selacholeic acid,[23] 15 16 tetracosenoic acid (24 C atoms, 1 double bond) appears to occur in traces in a number of fish oils

All the monoethenoid acids, as enumerated above, presumably have the *cis-* configuration In the case of oleic acid, decisive evidence for this configuration has been provided by the application of a number of independent physical methods That oleic acid is the *cis-* form of the acid may also be deduced from thermodynamic considerations The alternative form of the same acid (elaidic acid), which may be prepared artificially, has the higher melting point The higher melting, more stable isomer may generally be assumed to have the *trans-* form It has been pointed out[24] that the enzyme action within the living cell which is responsible for the elaboration of oils cannot be expected to yield isomers of the maximum thermodynamic stability

In vegetable oils, oleic acid is invariably associated with *linoleic* acid, 9·10, 12 13 octadecadienoic acid (18 C atoms, 2 double bonds) In the less unsaturated vegetable oils, it is subordinate in amount to oleic acid, but in the more unsaturated oils, such as soybean oil, linseed oil, perilla oil, etc , there is more linoleic than oleic acid It is ordinarily assumed that linoleic acid has the *cis-cis-* form

Although commonly referred to as "linoleic" acid, the octadecadienoic acid occurring in milk fats, most animal fats, and possibly fish oils, is not identical with ordinary linoleic acid derived from vegetable oils, since it does not yield the petroleum ether-insoluble bromides characteristic of the latter It is generally presumed that the octadecadienoic acid of milk fats and animal fats is a geometrical isomer of vegetable oil linoleic acid, but the precise difference between the two has yet to be determined Lard

[19a] R C Millican and J B Brown, *J Biol Chem* , **154**, 437–450 (1944)
[20] M Takano, *J Soc Chem Ind Japan*, **36**, 1317 (1933)
[21] Y Toyama and T Tsuchiya, *J Soc Chem Ind Japan*, **37**, 14B, 17B (1934)
[22] Y Toyama, *J Soc Chem Ind Japan*, **30**, 597–602 (1927)
[23] M Tsujimoto, *J Soc Chem Ind Japan*, **30**, 868–873 (1927)
[24] E F Armstrong and J Allan, *J Soc Chem Ind* , **43**, 207 218T (1924)

is different from other animal fats, such as beef and mutton tallows, in containing some quantity of the same form of linoleic acid as do vegetable oils This difference between lard and other animal fats is consistent with the ability of the hog to assimilate fats from vegetable sources with little change in their composition

Diethenoid acids of other than 18 carbon atoms are not believed to occur in nature

A hexadecatrienoic acid (16 C atoms, 3 double bonds) is believed to occur commonly in small amounts in marine oils According to Toyama and Tsuchiya,[25] the double bonds of the hexadecatrienoic acid in Japanese sardine oil are probably in the 6 7, 10 11, 14 15 positions This acid has been given the name, *hiragonic*

Linolenic acid, 9 10, 12 13, 15 16 octadecatrienoic acid (18 C atoms, 3 *double bonds*), *occurs in varying amount in some of the more* unsaturated vegetable oils In linseed and perilla oils, it is the principal fatty acid, *constituting 40%* or more of the total acids Apparently linolenic acid does not occur in either land or marine animal fats, although the presence *of an isomeric form* of this acid in fish oils is not strictly excluded by present evidence The only known nonconjugated natural octadecatrienoic acid other than linolenic acid is a 6 7, 9 10, 12 13 acid which is *confined to* the seeds of a single plant, the night candle plant, *Oenothara biennis*[26]

The positive identification of both octadecadienoic and octadecatrienoic acids has been rendered difficult by the circumstance that, in the past, the sole method available for their isolation has been the formation and separation of their insoluble bromine addition compounds Certain forms of these acids fail to yield insoluble bromides As mentioned above, the octadecadienoic acid of butter fat and tallows does not form an insoluble

acids partially isomerize during the bromination process It may be men tioned *in this connection that the terms* "alpha" or "beta" applied to linoleic or linolenic acids have no precise structural significance, but are used merely to designate the *forms which yield solid* and liquid bromides, respectively[27]

[25] Y Toyama and T Tsuchiya, *Bull Chem Soc Japan*, 10, 192–199 (1935)

[26] A Eibner L Widenmeyer and E Schild, *Chem Umschau Fette Öle Wachse Harze*, 34, 312 320 (1927)

[27] For detailed information concerning the isomerism of linoleic and linolenic acids and their bromo and hydroxy derivatives the reader is referred to the follow ing publications B H Nicolet and H L Cox *J Am Chem Soc* 44, 144–152 (1922) T Maruyama and Y Inoue and B Suzuki, *Proc Imp Acad Tokyo* 7, 15–18 (1931) T Maruyama and B Suzuki, *ibid*, 7, 379 (1931) T Maruyama, *J Soc Chem Ind Japan* 54, 1082–1087 (1933) J W McCutcheon *Can J Research* B16, 158–175 (1938) T G Green and T P Hilditch, *Biochem J*, 29, 1552 1563 (1935) R W Riemenschneider, D H

The low-temperature fractional crystallization technique for the isolation of linoleic and linolenic acids, recently developed by Brown and associates[28] may be expected eventually to yield more certain information concerning these compounds

Elaeostearic acid, 9·10, 11 12, 13 14 octadecatrienoic acid, is the conjugated isomer of linolenic acid It forms about 85% of the total fatty acids of tung oil, and is found also in certain other seed oils of the *Rosaceae*, *Euphorbiaceae*, and *Cucurbitaceae*, none of which are of present commercial importance

When long exposed to light or certain other isomerizing influences the natural "alpha" form of elaeostearic acid is transformed to a higher melting "beta" form, with consequent solidification of its glycerides The solvent extraction of tung oil produces glycerides of the "beta" form of the acid, which may, however, be permanently converted to those of liquid form by being heated to a high temperature [29] Differences in the two forms are believed to arise from *cis trans*- isomerism

Two other octadecatrienoic acids have been isolated which are believed to be geometric isomers of elaeostearic acid These are *punicic* acid, which occurs in pomegranate seed oil[30] and *trichosanic* acid which is found in the seed oil of the East Indian plant, *Trichosanthes cucumeroides* [31]

The single known instance of the occurrence in a vegetable oil of a fatty acid with more than three double bonds is *parinaric* acid, 9 10, 11 12, 13 14, 15 16 octadecatetraenoic acid (18 C atoms, 4 double bonds), which has been found in the seed oil of *Parinarium laurinum* [32]

A 4 5, 8 9, 12 13, 15 16 octadecatetraenoic (*moroctic*) acid has been reported in minor amounts in Japanese sardine oil[33] and the same acid or similar acids are believed to be found generally in marine oils

Both lard[34] and beef tallow[35] contain traces of *arachidonic* acid, eico-

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Wheeler, and C E Sando *J Biol Chem* 127, 391–402 (1939) J P Kass and G O Burr, *J Am Chem Soc* 61, 1062 1066 (1939) T P Hilditch and H Jasperson, *J Soc Chem Ind* 58, 233 241 (1939) A summary of present knowledge of the subject is presented by T P Hilditch (see footnote 1 page 4)

[28] J B Brown and G G Stoner *J Am Chem Soc*, 59, 3-6 (1937) J B Brown and J Frankel *ibid*, 60, 54–56 (1938) G Y Shinowara and J B Brown, *ibid*, 60, 2734-2738 (1938)

[29] W G Rose, A F Freeman, and R S McKinney, *Ind Eng Chem*, 34, 612–614 (1942)

[30] E H Farmer and F A van den Heuvel, *J Chem Soc*, 1936, 1809–1811

[31] Y Toyama and T Tsuchiya *J Soc Chem Ind Japan* 38, 182–185B (1935) H P Kaufmann J Baltes and J Buter *Ber* 70, 2535B (1937)

[32] E H Farmer and E Sunderland *J Chem Soc* 1935, 759 761 H P Kaufmann, J Baltes and S Funke *Fette u Seifen* 46, 302–304 (1938)

[33] Y Toyama and T Tsuchiya *Bull Chem Soc Japan* 10, 192–199 (1935)

[34] J B Brown and E M Deck *J Am Chem Soc*, 52, 1135–1138 (1930)

[35] J B Brown and C C Sheldon, *J Am Chem Soc*, 56, 2149 2151 (1934)

the unsaturated fatty acids are given in Table 4. The melting points of the unsaturated acids and their derivatives will be listed and discussed in later sections devoted to the chemical and physical properties of these materials.

(c) *Fatty Acids of Unusual Structure*

A fatty acid of low molecular weight constituting a major component of dolphin and porpoise oils was identified by André[46] as *isovaleric acid*, $(CH_3)_2\ CH \cdot CH_2 \cdot COOH$. Isovaleric acid is the sole natural fatty acid thus far discovered with an odd number of carbon atoms, and is also notable for its branched chain structure.

Tariric acid is a straight chain C_{18} acid with an acetylenic linkage or a triple bond between the 6th and 7th carbon atoms. It does not occur in any well-known fat or oil, apparently being confined to seed fat of the

TABLE 5

MOLECULAR WEIGHTS AND RELATED CHARACTERISTICS OF FATTY ACIDS OF UNUSUAL STRUCTURE

Fatty acid	Molecular weight of the acid	Molecular weight of its triglyceride	Neutralization value of the acid	Saponification value of the triglyceride	Iodine value of the acid	Iodine value of the triglyceride
Isovaleric	102.13	344.43	549.3	488.7	0	0
Ricinoleic	298.44	933.4	188 0	180.3	85.06	81.58
Licanic	292.39	915.22	191.9	183.9	—	—

Central and South American genus, *Picramnia*. According to Steger and van Loon,[47] the fat of *P. tariri* contains 89.8% of this acid.

A 6:7, 9:10 C_{18} acid with one double bond and one triple bond has been reported by Steger and van Loon as a major component of the seed fat of *Ongokea Gore*.[48] The relative positions of the double and triple bond in this acid were not determined.

Ricinoleic acid, 12-hydroxy 9:10 octadecenoic acid, is similar to oleic acid except that it has an hydroxyl group substituted for a hydrogen atom at the 12th carbon atom
fatty acids in castor
of this oil. There are a few plants related to the castor plant which apparently yield seed oils containing this acid, but none of the oils are produced commercially.

A dihydroxystearic acid of unknown configuration has been reported by

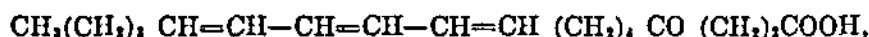
[46] E. André, *Bull. soc. chem.*, **35**, 857–868 (1924).

[47] A. Steger and J. van Loon, *Rec. trav chim.*, **52**, 593–600 (1933).

[48] A. Steger and J. van Loon, *Fette u. Seifen*, **44**, 243 (1937).

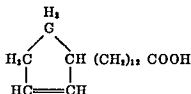
several investigators[49] as a minor or trace component of castor oil Dihydroxystearic acid has also been reported in traces in butterfat

Licanic acid occurs to the extent of about 70 to 75% of the total fatty acids in oiticica oil, from *Licania rigida*, and Mexican oiticicia or cacahuanache oil,[50] from *Licania arborea* Licanic acid has been shown by Brown and Farmer[51] to be 4-keto 9 10, 11 12, 13 14 octadecatrienoic acid,



hence is identical with elaeostearic acid but for the substitution of an oxygen atom for two hydrogen atoms, to form a keto- group at the 4th carbon atom Licanic acid is similar to elaeostearic acid in its tendency to isomerize to a higher melting isomer, or "beta" form

Chaulmoogric acid is a C_{18} monoethenoid acid characterized by a closed five-membered carbon ring at the end of the carbon chain



Hydnocarpic acid is similar to chaulmoogric acid, except that it is a C_{16} acid, *gorlic* acid differs from chaulmoogric acid in having a double bond between the 6th and 7th carbon atoms These three cyclic acids are confined to chaulmoogra oil and other seed oils of the *Flacourtiaceae* All are optically active

(d) *Artificial Fatty Acids*

Manufactured oil and fat products may in certain cases contain fatty acids which are not found in nature but are developed intentionally or unintentionally during processing treatments Some of the more important of these acids will be briefly mentioned

Elaidic acid is the *trans*- form of oleic acid It is usually formed in the laboratory by the treatment of oleic acid with oxides of nitrogen, but can also be produced by heating oleic acid in the presence of sulfur, selenium, etc

A variety of "iso-oleic" acids are formed during the catalytic hydrogenation of fats and oils Some of these apparently consist of elaidic acid Others are 12 13 monoethenoid acids produced by the hydrogenation of linoleic acid at the 9 10 double bond, or monoethenoid acids in which the double bond is in various positions other than the normal 9 10 position

[49] P Panjutin and M Rapoport, *Chem Umschau Fette Öle Wachze Härze*, **37**, 130–135 (1930) A Eibner and H Münzing (*Chem Abstracts*, **19**, 3027) H P Kaufmann and H Bornhardt, *Fette u Seifen*, **46**, 444–446 (1939)

[50] W G Rose and G S Jamieson, *Oil & Soap*, **20**, 227–231 (1943)

[51] W B Brown and E H Farmer, *Biochem J*, **29**, 631–639 (1935)

due to the wandering of double bonds from concurrent hydrogenation and dehydrogenation or other causes Some of these "iso-" acids have higher melting points than normal oleic acid Elaidic acid and others isomers of oleic acid are also produced in considerable quantity during the commercial sulfonation of oils

A 9 10, 11:12 conjugated octadecadienoic acid is formed in the dehydration of castor oil, and conjugated isomers of linoleic and linolenic acids are produced by commercial alkali isomerization of soybean, linseed, or other drying oils

3. Nonglyceride Components of Fats and Oils

The fats and oils of commerce all contain small amounts of various substances other than glycerides [52] Some of these are completely or substantially removed from the crude oils in the process of refining, and hence do not appear in most manufactured products. Of those which persist through refining treatment, some are without pronounced flavor, odor, or color, and are relatively inert from a chemical standpoint. These may be considered of minor importance, since their presence is neither objectionable nor desirable, insofar as most of the uses of the oils are concerned However, certain other components, particularly those which have antioxygenic properties, or are strongly flavored or highly colored, may considerably affect the character of the oil, even though they be present in no more than traces In the following section, the various nonglyceride components will be considered from the standpoint of their practical significance, rather than grouped and discussed on the basis of their chemical constitution

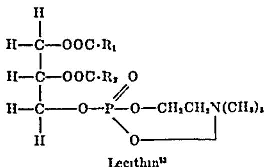
(a) *Substances Occurring Only in Crude Oils*

In the case of many fats and oils, the greater part of the nonglyceride portion is removed by hydration or combination with alkali in the course of ordinary refining The amount of removable nonglyceride substances varies considerably It is highest in certain seed oils, including particularly cottonseed, corn, and soybean oils, where it may constitute as much as 2% to 3% of the crude oil Other seed oils, for example, peanut oil and coconut oil, contain comparatively little of such materials, as do the common fruit pulp oils (olive oil and palm oil) Animal fats such as lard and edible tallow, which are derived from more or less pure fatty tissues, are very low in impurities of this class, although this may not be the case with fish oils, low-grade tallows or greases, or other animal fats rendered from entire carcasses or other stock containing much nonfatty tissue

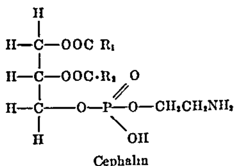
[52] For a comprehensive treatment of the minor components of fats and oils see G Hefter and H Schonfeld, *Chemie und Technologie der Fette und Fettprodukte*, Vol I, Springer, Vienna, 1936

The materials commonly removed (or largely removed) in refining may broadly described as consisting of phosphatides, carbohydrates and bohydrate derivatives, protein fragments, and various resinous and cilaginous materials of uncertain identity In addition, alkali refining noves any free fatty acids resulting from partial hydrolysis of the oil, and cts a partial removal of sterols, carotenoid pigments, etc

Phosphatides may be considered as triglycerides in which one fatty acid ical has been replaced with phosphoric acid In the class of phosphaes known as *lecithins*, the phosphoric acid is further esterified with cho-. In *cephalins*, the other common variety of phosphatides, the phosoric acid is similarly esterified with colamine, (hydroxyethylamine)



Lecithin[13]



Cephalin

Lecithins and cephalins occur together, in soybean phosphatides, for ample, the phosphatides consist of about 35% lecithins and 65% cephas[14] Lecithin and cephalin are distinguished from one another in mixres by the relative insolubility of the latter in ethyl alcohol As in the se of monoglycerides or other monosubstituted derivatives of the triycerides, there are both α- and β-forms of these compounds according to e position of the phosphoric acid group in the molecule

[13] According to P Karrer, *Organic Chemistry*, Nordeman, New York, 1938 For rther data concerning the structure of phosphatides, see H MacLean and I S acLean, *Lecithin and Allied Substances*, 2nd ed , Longmans, Green, London, 1937, d the recent review by E B Working and A C Andrews, *Chem Revs* , 29, 245–256 941)

[14] K S Markley and W H Goss, *Soybean Chemistry and Technology* Chem Pub , New York, 1944

In the case of vegetable oils, the fatty acids occurring in the phosphatides and the glycerides appear to be the same, except for certain highly unsaturated C_{20} and C_{22} acids which appear only in the phosphatides However, the proportions of the different acids in the two may be quite different The fatty acid compositions of the alcohol-soluble (lecithin) and alcohol-insoluble (cephalin) fractions of soybean and rapeseed phosphatides, as determined by Hilditch and Pedelty,[55] are given in Table 6 Analyses of the fatty acids from the total phosphatides of peanut and linseed oils, as reported by Hilditch and Zaky,[56] are shown in Table 7

Phosphatides usually occur to the extent of 1 to 2% in freshly extracted soybean or corn oils, although in the crude oils of commerce the greater part of the phosphatides will usually have been removed by water washing of the oil They are present in somewhat lesser amounts in other common

TABLE 6
FATTY ACID COMPOSITION OF SOYBEAN AND RAPESEED OIL PHOSPHATIDES[a]

Fatty acid	Soybean		Rapeseed[b]
	Alcohol insoluble %	Alcohol soluble %	Alcohol insoluble %
Myristic	—	—	0 8
Palmitic	11 7	17 3	8 3
Stearic	4 0	—	—
Arachidic	1 4	—	—
Hexadecenoic	8 6	5 5	2 1
Oleic	5 5	19 0[c]	22 4
Linoleic	63 3[d]	53 0[e]	42 2
Linolenic	—	3 7	trace
C_{20} unsaturated	5 5	1 5	22 7
Behenic	—	—	1 5

[a] T P Hilditch and W H Pedelty, *Biochem J*, **31**, 1964–1972 (1937)
[illegible] ble fraction
cids

seed oils The phosphatide content of most animal fats is very low See Table 8 The phosphorous content of refined and bleached peanut oils is of the order of 0 0001%, which would correspond to about 0 004% phosphatides

Raffinose and pentosans were found by Jamieson and Baughman[57] in considerable quantity in the mucilaginous material separating from crude cottonseed oil Carbohydrates in both free and combined forms appear to be generally associated with phosphatides in vegetable oils, and some workers are of the opinion that chemical combination may exist between the two McKinney, Jamieson, and Holton[58] detected what was believed to

[55] T P Hilditch and W H Pedelty, *Biochem J*, **31**, 1964–1972 (1937)
[56] T P Hilditch and Y A H Zaky, *Biochem J*, **36**, 815–821 (1942)
[57] G S Jamieson and W F Baughman, *J Oil & Fat Ind*, **3**, 347–355 (1926)
[58] R S McKinney, G S Jamieson and W B Holton, *Oil & Soap*, **14**, 126–129 (1937)

be a β glucoside-lecithin complex in soybean oil phosphatides However, the existence of such compounds is denied by Rewald,[59] who was apparently able to effect a quantitative separation of phosphatides from carbohydrates by treatment with suitable selective solvents A glucose-phytosterol complex (phytosteroline) was isolated by Jamieson and Baughman[57] from cottonseed oil

Certain protein degradation products are sufficiently soluble or dispersible in oil to appear in appreciable quantities in some fats and oils Their amount corresponds to the extent to which hydrolytic decomposition has

TABLE 7
FATTY ACID COMPOSITION OF PHOSPHATIDES FROM COTTONSEED, SUNFLOWER, PEANUT AND LINSEED OILS[a]

Fatty acid	Cottonseed %	Sunflower %	Peanut %	Linseed %
Palmitic	17 3	14 7	16 2	11 3
Stearic	7 3	5 1	2 8	10 6
Arachidic	2 8	9 5	—	—
Saturated C_{20} C_{22}, C_{24}	—	—	4 6	—
Sat C_{26}	—	—	2 5	—
Hexadecenoic	1 5	—	—	3 5
Oleic	20 3	19 3	47 1	33 6
Linoleic	44 4	45 9	22 7	20 4
Unsaturated C_{20} C_{22}	6 4	5 5	4 1	3 2

[a] T P Hilditch and Y A H Zaky, *Biochem J*, 36, 815–821 (1942)

TABLE 8
PHOSPHATIDE CONTENT OF VARIOUS CRUDE FATS AND OILS[a]

	Phosphatide content %
Soybean oil	1 1–3 2 (usually ca 1 8%)
Wheat oil	0 08–2 0
Butterfat, up to	1 4
Rice oil	0 5
Linseed oil	0 3
Sesame oil	0 1
Rapeseed oil	0 1
Beef fat, up to	0 07
Lard up to	0 05
Mutton fat	0 01

[a] H P Kaufmann, *Fette u Seifen* 48, 53 59 (1941)

occurred in the proteins of the seed or animal tissue from which the oil is extracted, and hence is largest in oil from damaged materials Both proteoses and peptones were found by Jamieson and Baughman[57] to occur in crude cottonseed oil

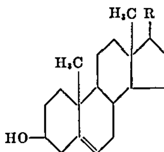
(b) Refined Oil Components of Minor Significance

Sterols are characteristic components of all fats and oils, comprising in most cases the greater part of the unsaponifiable matter However, they

[59] B Rewald, *Biochem Z*, 211, 199 201 (1929), *J Soc Chem Ind*, 56, 77 78T (1937)

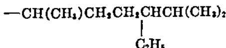
are ordinarily of little concern to the oil technologist, inasmuch as they are chemically inert and do not contribute to any important property of the oil Their recovery from oils is of some interest because they constitute starting materials for the synthesis of sex hormones and the artificial preparation of vitamin D, and have certain other therapeutic and pharmaceutical uses They may be separated from the other unsaponifiable constituents of fats through their solubility in hot alcohol, and may be concentrated from oils without saponification of the latter, by means of molecular distillation,[60] or extraction of the oil with alcohol or other suitable solvents Sterols occur in fats and oils both in the free form and as esters of the fatty acids Alkali refining of oils removes a portion of the sterols, hence the soapstock resulting from this operation constitutes a rich source of sterols [61] The recovery of sterols by adsorption from the oil on aluminum silicate has been proposed [62]

The characteristic sterol of animal fats is *cholesterol*, $C_{27}H_{46}O$, the sterols of vegetable oils apparently consist in most cases of a mixture of different members The vegetable oil sterols are known collectively as *phytosterols* Two phytosterols, β *sitosterol*, $C_{29}H_{50}O$, and *stigmasterol*, $C_{29}H_{48}O$, have been definitely characterized The structure of the sterols is represented as follows

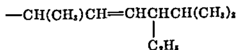


In the respective cases of the three sterols mentioned, the radical designated as *R* has the following forms





Cholesterol β Sitosterol



Stigmasterol

[60] The sterols have molecular weights in the range of *ca* 385 to 415, as compared with 800–900 for most triglycerides, they are correspondingly more volatile than the triglycerides

[61] E Holtz *Seifensieder Ztg*, 56, 140–141 (1928)

[62] H R Kraybill and M H Thornton U S Pat 2 225 275 (1940) H R Kraybill, M H Thornton and K E Eldridge *Ind Eng Chem* 32, 1138–1139 (1940)

γ-Sitosterol is considered as probably an isomer of β sitosterol "α Sitosterol," once thought to be another isomer, has been shown to be a mixture of at least three different compounds, which have been designated α_1, α_2- and α_3-

The sterols provide a means of distinguishing between fats of animal and of vegetable origin, since the melting point of cholesterol acetate (114°C) is substantially lower than that of the acetates of any of the phystosterols (126–137°C)[63] Admixtures of minor proportions of vegetable fats in animal fats may usually be detected, but the detection of animal fats in vegetable fats is less certain because of the variety of sterols occurring in the latter[64]

The sterol contents of a number of crude fats and oils, as given by Kaufmann,[65] are listed in Table 9

Most fats and oils contain appreciable amounts, e g, 0 1–0.2%, of hydrocarbons, which appear with the sterols in the unsaponifiable fraction

TABLE 9
STEROL CONTENT OF CRUDE FATS AND OILS[a]

	Sterol content %		Sterol content %
Halibut liver oil	7 6	Rapeseed	0 35
Wheat germ	3 6–6 7	Japanese fish oil	0 3
Cottonseed, up to	1 6	Poppyseed oil	0 25
Corn, up to	1 2	Peanut oil	0 25
Rice bran oil	0 75	Cocoa butter	0 2
Soybean	0 7–0 8	Olive oil	0 13
Sesame	0 6	Lard	0 12
Castor	0 5	Mutton tallow	0 1
Butterfat, up to	0 5	Coconut oil	0 08
Linseed	0 4	Beef tallow	0 08

[a] H P Kaufmann, *Fette u Seifen*, 48, 53 59 (1941)

Squalene, $C_{30}H_{50}$, a highly unsaturated hydrocarbon structurally related to the carotenes, is found in large quantities in some fish liver oils, and has been reported in fractional percentages (0 1–0 7%) in olive, rice bran, and wheat germ oils and in lesser amounts in many other oils[66] *Gadusene*, $C_{18}H_{32}$, another unsaturated hydrocarbon, has been isolated from fish liver, rice, and soybean oils[67] Several other hydrocarbons, *pristane*, *zamene*, *celorhinene*, etc, have been found in fish or fish liver oils Although

[63] The melting point of the mixed acetates of the sterols of vegetable oils is usually over 125°C although there are some exceptions to this rule

[64] For detailed information concerning the detection of animal-vegetable fat mixtures see the monograph of G S Jamieson *Vegetable Fats and Oils* 2nd ed, Reinhold, New York, 1943

[65] H P Kaufmann, *Fette u Seifen*, 48, 53–59 (1941)

[66] K Taufel, H Heinisch, and W Heimann, *Biochem Z*, 303, 324–328 (1940) J Fitelson, *J Assoc Official Agr Chem*, 26, 506–511 (1943)

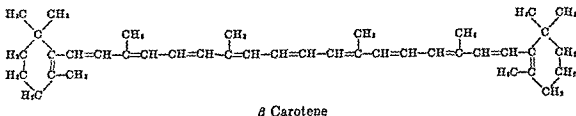
[67] J Nakamiya, *Sci Papers Inst Phys Chem Research (Tokyo)*, 28, 16–26 (1935)

the hydrocarbons are classed here with the neutral components of fats and oils, the possibility that some of these substances may affect the stability or flavor and odor of the oils is not to be excluded

Fatty alcohols, both in the free state and in combination with fatty acids as waxes, are found in quantity in many marine oils, but do not occur to any important extent in land animal or vegetable oils However, some vegetable oils, including linseed, corn, and soybean oils contain sufficient quantities of wax to cause them to cloud when chilled to a low temperature Corn oil wax was examined by Shriver, Nabenhauer, and Anderson,[68] who found it to consist of a mixture of the esters of myricyl alcohol with *n* lignoceric and *iso*-behenic acids However, Jamieson[69] reported that a sample of corn oil wax examined by him consisted principally of the esters of cetyl alcohol Earle and Detwiler[70] found the wax of soybean oils to consist of a complex mixture of esters The principal alcohols ranged from $C_{3?}$ to below C_{28} while the acids had an average chain length of C_{22} The wax amounted to no more than 0 002% of the oil

(c) *Components Affecting the Appearance of Oils*

The characteristic yellow-red color of most fats and oils is due to the presence of various carotenoid pigments Structurally, the carotenoids consist of highly unsaturated hydrocarbon chains, or isoprene units, arranged in various cyclic and acyclic configurations The following structure, proposed by Karrer[71] for β-carotene, is representative



β Carotene

Ordinary hydrogenation of an oil will reduce the unsaturation of its carotenoid pigments sufficiently to effect a significant reduction in color These pigments are also unstable to heat, hence oils are bleached by high temperature treatment, as in steam deodorization Their chromogenic properties may be destroyed by oxidation, although ordinarily appreciable bleaching of an oil does not occur until oxidation has progressed to the point of producing rancidity or near rancidity Limited oxidation ordinarily darkens vegetable oils This darkening has recently been shown by

[68] R L Shriver, F P Nabenhauer, and R J Anderson *J Am Chem Soc*, 49, 1290-1294 (1927)

[69] G S Jamieson *Vegetable Fats and Oils* 2nd ed, Reinhold, New York, 1943, p 180

[70] F R Earle and S B Detwiler, *Oil & Soap*, 18, 117-119 (1941)

[71] P Karrer, *Organic Chemistry* Nordeman, New York, 1938

Golumbic[72] to be due to the production of chroman-5,6-quinones (compounds related to the tocopherols) from colorless precursors, rather than to reactions involving the carotenoids The carotenoids are readily adsorbed by Fuller's earth and activated carbon, hence the color of an oil pigmented solely by these compounds may be reduced to any desired value by sufficiently intensive treatment with adsorbents Palm oil is much the highest of the various oils in carotenoid pigments, containing 0 05% to 0 20% of β-carotene [65]

Certain fats and oils, notably olive oil, soybean oil derived from green beans, and some inedible tallows, have a greenish color from the presence of chlorophyll or related compounds Except in olive oil, a green color is generally undesirable Green color in oils is not reduced by hydrogenation—in fact hydrogenation has the apparent effect of intensifying the green color because of its reduction of the reds and yellows of the carotenoids—and is relatively difficult to remove by bleaching with adsorbents

Certain brownish pigments, which do not appear in oils of good quality, but may be found in oils derived from damaged materials, appear to be decomposition products of proteins, carbohydrates, etc Some of these are exceedingly difficult to remove by ordinary processing methods

(d) *Components Affecting the Stability of Oils*

It has long been recognized that, due to their content of minute amounts of substances capable of powerfully inhibiting oxidation, natural fats and oils are much more resistant to oxidative deterioration than are pure triglycerides In spite of notable contributions to the knowledge of oil and fat antioxidants in recent years, both the nature and the mode of action of these substances are still but imperfectly understood [73]

One important class of antioxidants of almost universal distribution consists of the tocopherols, which are identical with vitamin E and were first isolated and characterized by workers in the field of nutrition The tocopherols, discovered and named by Evans and co-workers,[74] were demonstrated by Olcott and Emerson[75] to be effective antioxidants, and to be the active substances in the "inhibitols" previously isolated from a variety of vegetable oils by Olcott and Mattill [76] Three different tocopherols have

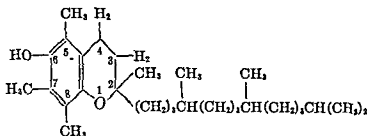
[72] C Golumbic, *J Am Chem Soc*, **64**, 2337–2340 (1942)

[73] A recent review of vegetable oil antioxidants has been furnished by H S Olcott and H A Mattill, *Chem Revs*, **29**, 257–268 (1941) For reviews of the chemistry of the tocopherols see L I Smith, *Chem Revs*, **27**, 287–329 (1940) and W John, *Ergeb Physiol biol Chem exptl Pharmakol*, **42**, 1–52 (1939)

[74] H M Evans O H Emerson, and G A Emerson, *J Biol Chem*, **113**, 319–332 (1936) O H Emerson, G A Emerson, A Mohammad, and H M Evans, *ibid*, **122**, 99 107 (1937)

[75] H S Olcott and O H Emerson, *J Am Chem Soc*, **59**, 1008–1009 (1937)

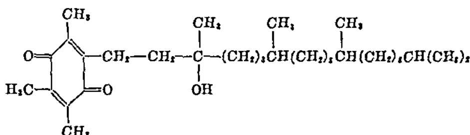
[76] H S Olcott and H A Mattill, *J Am Chem Soc*, **58**, 1627–1630 (1936)



α-Tocopherol

been identified, and designated as α-, β-, and γ-; β- and γ-tocopherols differ from α-tocopherol in having one less methyl group substituted in the benzene ring. In β-tocopherol the methyl groups are in the 5 and 8 positions, and in γ-tocopherol they are in the 7 and 8 positions.

Like other antioxidants, the tocopherols are themselves readily oxidizable. Mild oxidation of a tocopherol opens the heterocylic ring, to form



α Tocoquinone

tocoquinone, which is not an antioxidant. γ-Tocopherol has been shown by Olcott and Emerson[75] to be a more effective antioxidant than β-tocopherol, which is in turn more effective than α-tocopherol.

Entirely trustworthy assays for the tocopherols present in different oils are generally lacking because of the fact that there is no quantitative method which is specific for these substances. Two relatively simple colorimetric methods for the estimation of total tocopherols are in general use. Of these, the Furter-Meyer test[77] responds not only to tocopherols, but also to other compounds of related structure, notably tocoquinones, and thus is inclined to yield somewhat high values, particularly in the examination of oils which have suffered some degree of oxidation prior to the test. The Emmerie-Engel method[78] depends upon the ability of tocopherols to reduce ferric chloride, and hence may be influenced by the pres-

[77] M. Furter and R. E. Meyer, *Helv. Chim. Acta*, **22**, 240–250 (1939). The modification of the Furter Meyer method due to F. W. Quackenbush, H. L. Gottlieb, and H. Steenbock, *Ind. Eng. Chem.*, **33**, 1276–1278 (1941), is generally considered more satisfactory than the original method.

[78] A. Emmerie and C. Engel, *Rec. trav. chim.*, **57**, 1351–1355 (1938). The modified method of W. E. Parker and W. D. McFarlane, *Can. J. Research*, **18**, 405–409 (1940), is generally used in preference to the original Emmerie Engel method, which is inaccurate in the presence of fat peroxides.

ence of other substances which are capable of being easily oxidized or reduced

The different tocopherols may be qualitatively differentiated after conversion to the crystalline allophonates by treatment with cyanic acid Melting points of the allophonates of α, β, and γ-tocopherols are 158–160°, 144–146°, and 138–140°C, respectively

Tocopherols appear in the unsaponifiable fraction of fats and oils [79] Tocopherol concentrates may be prepared from oils without saponification of the latter by the techniques of molecular distillation[80] or low-temperature fractional crystallization [81] Mixtures of the tocopherols in such concentrates are most efficiently resolved by chromatography [82]

β-Tocopherol has been found only in wheat germ oil[74], the tocopherols of most vegetable oils appear to consist of a mixture of α- and γ-tocopherols [74, 83] Selected analyses of different oils and fats for tocopherol content are listed in Table 10

TABLE 10
TOCOPHEROL CONTENT OF FATS AND OILS
(ANALYSES BY MODIFIED EMMERIE ENGEL METHOD)

Oil	Tocopherols %	Oil	Tocopherols %
Babassu, crude	0 003	Peanut, crude	0 052
Castor	0 05	refined	0 048
Coconut, refined	0 003	Pecan, refined	0 045
Corn, refined	0 095	Rice bran, crude	0 100
Cottonseed, crude	0 110	refined	0 090
refined	0 090	Safflower crude	0 080
Lard, prime steam	ca 0 0005	Sesame, refined	0 050
Oleo oil	ca 0 002	Soybean, refined	0 110
Olive	0 020	Wheat germ crude	0 40
Palm, crude	0 050	solvent extracted	0 55

Although the tocopherols may be considered the chief antioxidants of vegetable oils, there are undoubtedly others as yet unidentified In this connection sesame and rice bran oils are of particular interest These oils, particularly after hydrogenation, are significantly more stable than such oils as cottonseed, soybean, or peanut oils of equivalent unsaturation The tocopherol content of these oils is not unusually high, and in any case it

[79] However, special precautions must be observed if they are to be recovered unchanged from saponified oils

[80] K C D Hickman, *Ind Eng Chem*, **32**, 1451–1453 (1940)

[81] W S Singleton and A E Bailey, *Oil & Soap*, **21**, 224–226 (1944)

[82] J G Baxter, C D Robeson, J D Taylor, and R W Lehman, *J Am Chem Soc*, **65**, 918–924 (1943), have prepared in a pure form and examined, with respect to their melting points and spectral characteristics, the three tocopherols and a number of their esters

[83] O H Emerson, G A Emerson, and H M Evans, *Science*, **89**, 183 (1939)

has been demonstrated[84] that extremely high stability is not imparted to an oil simply by a high tocopherol content, since the tocopherols exhibit their maximum effect at relatively low levels of concentration Hence the high stability of sesame and rice bran oils is evidently due to the presence of antioxidants more potent than tocopherols [85]

An example of a phenolic-type antioxidant other than tocopherols, but related to these compounds, is to be found in the chroman-5,6-quinones isolated by Golumbic[72] from partially oxidized vegetable oils The work of Swift, Mann, and Fisher[86] has indicated that the chroman-5,6-quinones are derived from γ-tocopherol, by oxidation Gossypol, a complex phenolic substance occurring in crude, but not in refined, cottonseed oil has been shown by Royce[87] to have strong antioxygenic properties The natural antioxidants appear to be generally high in molecular weight and non-volatile, since they largely persist through the rather drastic treatment of high-temperature steam deodorization [88]

O H$_2$
O= —H$_2$
CH$_3$ CH$_3$ CH$_3$
H$_3$C— O (CH$_2$)$_3$CH(CH$_2$)$_3$CH(CH$_2$)$_3$CH(CH$_3$)$_2$
CH$_3$

Chroman 5,6 quinone

Phosphatides are not antioxidants when present alone in oils, but some phosphatides are capable of reinforcing the action of tocopherols or other antioxidants of the phenolic type In commercial preparations of mixed phosphatides, Olcott and Mattill[89] have shown that antioxygenic activity

[84] See, for example, G D Oliver, W S Singleton, and A E Bailey, *Oil & Soap*, **21**, 188 193 (1944)

[85] Sesamol, a phenolic compound appearing in sesame oil in the form of a glucoside, sesamoline, has been reported by H S Olcott and H A Mattill, *Chem Revs* , **29**, 257-268 (1941), to have antioxygenic properties

[86] C E Swift, G E Mann, and G S Fisher, *Oil & Soap*, **21**, 317-320 (1944)

[87] H D Royce, *Oil & Soap*, **10**, 123-125 (1933) H D Royce and F A Lindsey, *Ind Eng Chem* , **25**, 1047-1050 (1933)

[88] However, there is some loss of tocopherols and other antioxidants from oils during the process of deodorization See, for example, D P Grettie (to Industrial Patents Corp), U S Pat 2,095,740 (1937), and also the following series of U S Pats issued in 1944 and assigned to Distillation Products, Inc K C D Hickman 2 349 - 269-70, 2,349,274-78, 2,349,590, and 2,349,789, *K C D Hickman and N H Kuhrt*, 2,349,273, J G Baxter, 2,349,273, J G Baxter and C D Robeson, 2,349,273, J G Baxter and J D Taylor, 2 350,713

[89] H S Olcott and H A Mattill, *Oil & Soap*, **13**, 98-100 (1936)

is confined to the cephalin fraction Phosphoric acid and other acids and acid substances similarly reinforce the action of phenolic antioxidants, and the antioxygenic activity of cephalin, in contrast to the lack of activity of lecithin, is attributed to the presence in the former of a free hydroxyl group of phosphoric acid The reinforcing or synergistic action of cephalin, like that of other acid inhibitors, is lost when the fat is subjected to an alkaline environment, as it is for example when incorporated into biscuits, crackers, or other baked goods

Evidence relative to the antioxidant or pro-oxidant effect of carotene, chlorophyll, xanthophyll, and other pigments in fats and oils is somewhat conflicting However, as pointed out by Markley,[54] any pigment may be expected to influence the oxidation of fats, through its ability to absorb photochemical energy in the form of light, and thus supply the energy necessary for the activation and subsequent oxidation of fat molecules Conceivably, pigments which are neutral or even antioxidant in the dark may act as pro-oxidants in the presence of light

(e) *Components Contributing to Flavor and Odor*

Relatively few of the compounds responsible for the flavor and odors of fats and oils have been identified Certain ketones of high molecular weight were isolated from lauric acid-type oils by Haller and Lassieur[90] and Salway,[91] and from soybean oil by Schmalfuss and Treu [92] Some of the hydrocarbons in vegetable oils appear to be strongly odoriferous The odoriferous components of vegetable oils are as a whole somewhat remarkable for their low volatility Complete deodorization of most oils requires prolonged vacuum steam distillation at a highly elevated temperature, *e g*, 200–250°C

Certain types of flavors and odors in fats are not due simply to the presence of volatile and consequently removable components, but are intimately related to the actual glycerides of the oils In fish oils, in particular, it will be observed that the characteristic odor of the oils is not permanently removable by even the most drastic steam deodorization, but is recurrent upon slight oxidation of the oil According to the investigations of Davies and Gill,[93] fishiness is associated with the concurrent presence in the oil of nitrogenous compounds and highly unsaturated glycerides, and results from the chemical combination of the two during oxidation of the glycerides

[90] A Haller and A Lassieur, *Compt rend*, **150**, 1013 1019 (1910), **151**, 697–699 (1911)

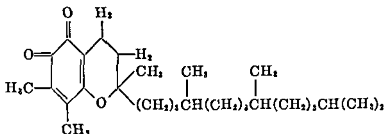
[91] A H Salway, *J Chem Soc*, **111**, 407–410 (1917)

[92] H Schmalfuss and A Treu, *Biochem Z*, **189**, 49 (1927)

[93] W L Davies and E Gill, *J Soc Chem Ind*, **55**, 141–146T (1936)

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[89] H S Olcott and H A Mattill, *Oil & Soap*, **13**, 98–100 (1936)

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[92] H Schmalfuss and A Treu, *Biochem Z*, **189**, 49 (1927)

[93] W L Davies and E Gill, *J Soc Chem Ind*, **55**, 141–146T (1936)

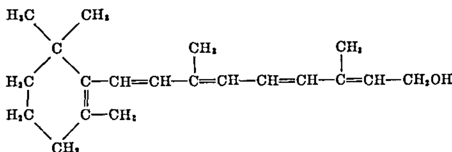
Flavor development in deodorized fats as a result of limited oxidation is commonly termed "flavor reversion" It occurs in certain vegetable and land animal fats, as well as in fish oils, but is pronounced only in fats which contain fatty acids with more than two double bonds

Peculiarly, a tendency to "revert" in flavor persists in soybean, linseed, and other linolenic acid oils after these oils have been hydrogenated to a degree which is apparently sufficient to eliminate all trienoic acids completely In the hydrogenated fats it would appear, therefore, that linolenic acid is the precursor of a hydrogenated compound responsible for flavor reversion It has recently been postulated by Lemon[93a] that this hypothetical compound is 9 10, 15 16 *octadecadienoic acid produced by hydrogenation* of linolenic at the 12 13 double bond It is of course possible that the actual flavor in question is produced by interaction of such an isomer with certain nonglyceride substances in the oil, some of the latter may be peculiar to soybean and linseed oils

(*f*) *Components of Nutritional Significance*

Fats and oils are important sources of the fat-soluble vitamins, A, D, and E

Vitamin A may be considered to be derived from β carotene (see page

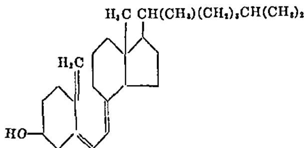


Vitamin A

28) by fissure of a molecule of the latter in the middle of the hydrocarbon chain, and the addition of one molecule of water to each fragment Such conversion of β carotene to vitamin A does in fact occur in the body of man and other animals, hence β carotene is designated as provitamin A The proportion of the provitamin actually converted to the vitamin in the human body is not certainly known, but appears to be not greater than about one half Certain other carotenoid pigments for example, γ carotene, also yield vitamin A, but many do not, hence the depth of color in a fat is not a certain indication of its provitamin content although in some fats, including butter, there is a rough correlation between the two

[93a] See J G Armstrong and W D McFarlane *Oil & Soap* **21**, 322–327 (1944)

Vitamin D has had ascribed to it the following formula



Natural vitamin D

It is therefore related to the sterols (see page 26), its condensed ring system differing from that of the sterols in having the second benzene ring opened A second form of vitamin D, called calciferol, can be prepared by the irradiation of ergosterol, or by the irradiation of cholesterol after suitable chemical treatment This form has the same ring structure as that depicted above, but has a slightly different side chain It is probable that there are in addition other forms of this vitamin

Butter contains from 0 0003–0 0015% of vitamin A, in addition to an approximately equal amount of β-carotene [94] Oleo oil contains an appreciable amount of carotene, and palm oil has a very high content of this pigment Most other vegetable oils appear to contain no important amount of either vitamin A or its provitamins, their yellow-red color apparently being derived from carotenoid pigments other than the precursors of vitamin A

Butter also contains from 0 1 to 1 0 International Unit of vitamin D per gram[95], the content of this vitamin, like that of vitamin A, being highest in the summer and lowest in the winter Land animals fats and vegetable oils contain no appreciable amounts of vitamin D

The body oils of most fishes and marine animals contain considerable amounts of vitamins A and D, for example about 500 and 100 U S P units per gram, respectively, in the case of sardine, herring, and menhaden oils Certain fish liver oils are extremely rich in these vitamins Halibut, swordfish, tunny, and shark liver oils have been reported to contain 100,000

[94] The biological activity, in terms of International Units, is dependent upon the content of carotene as well as that of vitamin A By definition, 0 6 μg β carotene = 1 I U One gram of pure vitamin A is now believed to be equivalent to approximately 4,000,000 I U (see J G Baxter and C D Robeson, *J Am Chem Soc*, **64**, 2407–2410 (1942) and K Hickman, *Ann Rev Biochem*, **12**, 353–396 (1943)) Hence, if C = carotene content in μg per g and A = vitamin A content in μg per g, I U per g = $1.67C + 4A$ For further information concerning the vitamin A activity of butter, see pages 135–137

[95] 1 I U is equivalent in biological activity to 0 025 μg calciferol

to 300,000 U S P units of vitamin A per gram,[96] and vitamin D contents as high as 70,000 U S P units per gram have been reported in tuna liver oils

However, fish liver oils of very high vitamin A potency are not generally available in quantity, and the vitamin A concentrates of commerce are principally obtained from oils of low to medium vitamin A content, such as dogfish and grayfish liver oils These oils generally contain 10,000 to 15,000 U S P units of vitamin A per gram In fish liver oils vitamin A appears to exist principally in the form of fatty acid esters

The subject of vitamin E in oils has been covered in the previous discussion of tocopherols (page 30), with which this vitamin is identical

Following the demonstration by Burr and co-workers[97] that rats developed symptoms of a nutritional deficiency on diets devoid of linoleic acid, there has been much discussion of the question of essential fatty acids in the human diet The indispensability of such acids is still unsettled Human subjects on similar diets, or on diets virtually devoid of fat of any kind have failed to evince symptoms of any dietary deficiency, on the other hand, there is no evidence that the human body is able to synthesize the highly unsaturated acids which are essential constituents of many vital body cells The issue is, however, somewhat academic, since such acids are so widely distributed as to render any deficiency in the normal diet virtually out of the question

[96] 1 g pure vitamin A = approximately 4 000,000 International or U S P units hence the vitamin A content of an oil containing 100,000 U S P units per g is about 2 5%

[97] G O Burr and M M Burr, *J Biol Chem* , **82**, 345–367 (1929), *ibid* , **86**, 587–621 (1930) G O Burr, M M Burr, and E S Miller, *ibid* , **97**, 1 9 (1932)

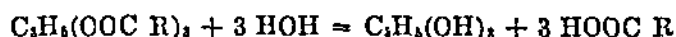
CHAPTER II

REACTIONS OF FATS AND FATTY ACIDS

There are certain reactions of fats and fatty acids which are of particular importance because they are employed in the manufacture of fatty products, are involved in the utilization or deterioration of fats and oils, or form the basis for common analytical methods A number of these reactions are discussed at length in the individual chapters devoted to specific unit processes This chapter will be devoted principally to reactions not given detailed consideration elsewhere although, for the sake of completeness, all the more important reactions will be briefly mentioned

1 Hydrolysis and Related Reactions

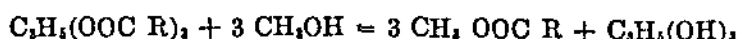
Under the proper conditions, the triglycerides of fats and oils may be hydrolyzed, to yield free fatty acids and glycerol



$$C_3H_5(OOC\cdot R)_3 + 3\ HOH \rightleftharpoons C_3H_5(OH)_3 + 3\ HOOC\cdot R$$

The reaction is reversible, if reactants and reaction products are not removed from the sphere of reaction, an equilibrium depending upon the concentrations of the former will eventually be reached In practical fat splitting, a high degree of hydrolysis is insured by the provision of a large excess of water On the other hand, if the reverse reaction is the one desired, it may be made substantially complete by continuously removing water from the reaction zone By causing hydrolysis to take place, and then substituting another alcohol for glycerol in the reverse, or esterification reaction, fatty acid esters of any mono-, di-, or polyhydric alcohol may readily be formed

Esters of the lower alcohols, *i e*, methyl and ethyl alcohol, may also be prepared by directly reacting the alcohol with the fat to displace glycerol



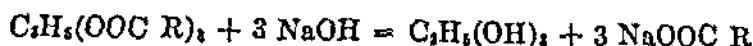
$$C_3H_5(OOC\cdot R)_3 + 3\ CH_3OH \rightleftharpoons 3\ CH_3\cdot OOC\cdot R + C_3H_5(OH)_3$$

Low molecular weight acids of the fatty acid series can be made to displace high molecular weight fatty acids from glycerides by an analagous reaction

In the presence of an excess of free glycerol or other alcohol, which may be added to the fat, or formed in the fat by partial hydrolysis, the different fatty acids in the triglyceride molecules can be made to undergo shifts of position, not in a directed manner, but at random, with the eventual formation of new glycerides differing in structure from the old

All the preceding reactions have commercial applications, and are discussed more fully on pages 666–686

If the fat is split, not with the aid of water, but with an alkali, to yield glycerol and a salt or soap of the alkali metal, the reaction is termed saponification


$$C_3H_5(OOC\ R)_3 + 3\ NaOH = C_3H_5(OH)_3 + 3\ NaOOC\ R$$

This reaction, which forms the foundation of the soapmaking industry, is discussed on pages 623–635

Soaps may of course also be made by reacting the free acids with the alkali, water being set free in the reaction Soaps of the heavier metals are made by reacting the free acids with the metal oxide or hydroxide, or by double decomposition of a sodium or potassium soap and a salt of the metal The following reaction is typical of the latter method


$$2\ NaOOC\ R + Pb(OOC\ CH_3)_2 = Pb(OOC\ R)_2 + 2\ NaOOC\ CH_3$$

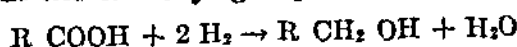
The *acid value* is a measure of the hydrolysis that has occurred in a fat, and is defined as the number of milligrams of potassium hydroxide required to neutralize the free fatty acids in one gram of fat The acidity of fats is also often expressed directly in terms of *percent free fatty acids,* the assumption usually being made in the calculation that the acids have a molecular weight equal to that of oleic acid The relation between acid value and percent free fatty acids calculated as oleic is as follows 1 unit of acid value = 0 503% free fatty acids

The *saponification value* is the number of milligrams of potassium hydroxide required to saponify one gram of fat The *neutralization value* is the number of milligrams of potassium hydroxide required to neutralize one gram of fatty acids The *saponification equivalent* is the number of grams of material saponified by one mole, or 56 104 grams of potassium hydroxide It is thus numerically equal to the mean molecular weight of the fatty acids, if the material consists of acids, or equal to one-third the mean molecular weight of the glycerides, if it is assumed that the material consists entirely of neutral oil, free of unsaponifiable matter or other impurities The *ester value* is the number of milligrams of potassium hydroxide required to saponify the neutral oil in a one gram sample, exclusive of that required to neutralize any free acids, and hence is equal to the saponification value minus the acid value The following relation holds between the saponification value and the saponification equivalent (saponification value) (saponification equivalent) = 56,104

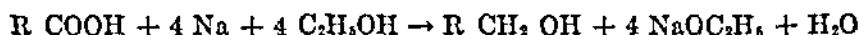
2 Other Reactions Involving the Carboxyl Group

(a) *Hydrogenation in the Carboxyl Group*

Reacted under the proper conditions with a suitable catalyst, fatty acids can add hydrogen in the carboxyl group to form fatty alcohols


$$R\ COOH + 2\ H_2 \rightarrow R\ CH_2\ OH + H_2O$$

Fatty alcohols may also be prepared by the sodium reduction of fatty acids in alcohol



$$R\ COOH + 4\ Na + 4\ C_2H_5OH \rightarrow R\ CH_2\ OH + 4\ NaOC_2H_5 + H_2O$$

Both of the above reactions are used in the commercial preparation of fatty alcohols (see pages 618–621)

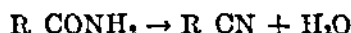
(b) *Formation of Nitrogen Derivatives*

Fatty acids react with ammonia to form amides [1]



$$R\ COOH + NH_3 \rightarrow R\ CONH_2 + H_2O$$

Amides undergo dehydration at an elevated temperature to form the corresponding nitriles

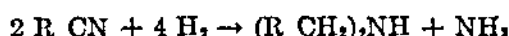


$$R\ CONH_2 \rightarrow R\ CN + H_2O$$

Upon catalytic hydrogenation, nitriles are converted into the corresponding primary or secondary amines



$$R\ CN + 2\ H_2 \rightarrow R\ CH_2\ NH_2$$



$$2\ R\ CN + 4\ H_2 \rightarrow (R\ CH_2)_2NH + NH_3$$

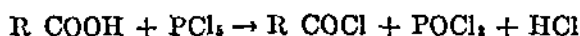
The preceding reactions are all utilized in the commercial production of nitrogen-containing fatty acid derivatives

(c) *Formation of Acid Chlorides*

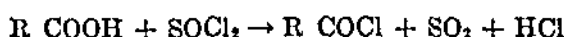
Acid chlorides may be prepared by reacting fatty acids with various reagents, of which phosphorus trichloride, PCl_3, phosphorus pentachloride, PCl_5, thionyl chloride, $SOCl_2$, and oxalyl chloride, $(COCl)_2$, are the ones most commonly employed



$$3\ R\ COOH + PCl_3 \rightarrow 3\ R\ COCl + H_3PO_3$$



$$R\ COOH + PCl_5 \rightarrow R\ COCl + POCl_3 + HCl$$

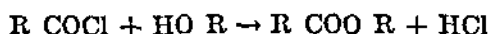


$$R\ COOH + SOCl_2 \rightarrow R\ COCl + SO_2 + HCl$$

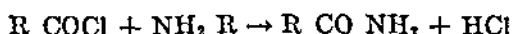


$$R\ COOH + (COCl)_2 \rightarrow R\ COCl + HCl + CO_2 + CO$$

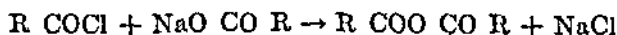
Although the acid chlorides are not prepared technically in large quantities, they are of considerable importance in oil and fat chemistry, inasmuch as they serve as intermediates for the production of synthetic glycerides and waxes, and a wide variety of other fatty acid derivatives The chlorine atom is highly labile, and readily replaced by a number of other groups The following reactions are typical



$$R\ COCl + HO\ R \rightarrow R\ COO\ R + HCl$$



$$R\ COCl + NH_2\ R \rightarrow R\ CO\ NH_2 + HCl$$



$$R\ COCl + NaO\ CO\ R \rightarrow R\ COO\ CO\ R + NaCl$$

[1] V F Balaty, L L Fellinger, and L F Audrieth, *Ind Eng Chem*, **31**, 280–282 (1939)

3. Reactions in the Fatty Acid Chain

Most of the reactions which occur in the fatty acid chains involve addition at the double bonds of unsaturated fatty acids, although in a few cases substitution may occur in saturated acids, with the replacement of hydrogen atoms by other atoms or groups In general, reactions of this type occur with more or less equal facility in the free acids, the glycerides, or other esters or salts of the acids

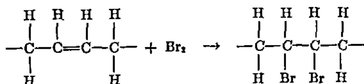
(a) *Hydrogenation*

In the presence of a suitable catalyst, gaseous hydrogen is readily added at the double bonds of unsaturated fatty acids, to transform these acids to the corresponding saturated acids, or to reduce their degree of unsaturation Catalytic hydrogenation is carried out commercially on a very wide scale, as described on pages 558 *et seq*

Theoretically, the hydrogen absorption is the best index of the degree of unsaturation in a fat, inasmuch as hydrogen is added quantitatively at the double bonds, without the possibility, as in halogen addition, etc , of addition being incomplete, or of substitution or other side reactions occurring However, the *hydrogen number* of fats is seldom determined as an analytical characteristic, due to the mechanical difficulties in carrying out accurate measurements of hydrogen absorption

(b) *Halogenation*

Chlorine, bromine, and iodine, and also iodine monochloride and iodine monobromide may be added at the double bonds of unsaturated acids, as in the following example



Addition takes place readily, but is quantitative or nearly quantitative only under special conditions, due to the tendency of the halogen to add incompletely or, in other cases, to displace hydrogen atoms

The quantitative addition of iodine monobromide or iodine monochloride forms the basis of the *iodine value*, which is defined as the number of grams of iodine absorbed under standard conditions by 100 grams of fat The iodine value represents the true unsaturation of fats or fatty acids only when the double bonds in the latter are unconjugated, halogen absorption is not quantitative in the case of conjugated fatty acids

Since the bromine addition compounds of unsaturated fatty acids tend to become less soluble in cold ether and petroleum ether as the number of

double bonds increases, mixed fatty acids are often brominated for the purpose of estimating or detecting the presence of highly unsaturated acids The *hexabromide number* is the number of grams of insoluble bromides obtained from 100 grams of fatty acids under certain standard conditions Once believed to indicate quantitatively the percentage of linolenic acid in the sample, it is now known to be influenced by the contents of both oleic and linoleic acid

Halogenation may also occur by substitution, with free or combined halogens replacing one or more hydrogen atoms in the hydrocarbon chain Although substitution occurs most readily at the carbon atom next to the carboxyl group, it is in most cases impossible to predict either the extent of substitution or the positions at which substitution will occur Halogenation by substitution does not occur readily except under special conditions, such as prolonged exposure of the fat to an excess of halogen in certain solvents, or exposure to halogens in the presence of a catalyst, such as phosphorous

(c) *Addition of Thiocyanogen and Maleic Anhydride*

Analytical methods involving the addition of thiocyanogen and maleic anhydride have been developed to provide more information concerning the composition of fats than is yielded by iodine values alone Thiocyanogen (SCN) was formerly believed to add quantitatively to one of the two double bonds of a diunsaturated acid and two of the three double bonds of a triunsaturated acid It is now known that the actual addition depends upon the conditions under which reaction takes place (see page 169), but the extent of addition may be made reproducible by standardizing the conditions, hence this reaction constitutes the basis of a valuable analytical method The *thiocyanogen value* is analogous to the iodine value, being calculated in terms of iodine, on the same basis as the iodine value

The Diels-Alder reaction (see p 374), in which maleic anhydride reacts with conjugated fatty acids, is the basis of the *diene value*, which like the thiocyanogen value is calculated in terms of equivalents of iodine The theoretical diene value of trielaeostearin is 87 2 However, it has been shown[2] that the actual diene value of conjugated acids, like the thiocyanogen value of unsaturated acids, is variable according to the conditions of reaction

(d) *Addition of Sulfuric Acid*

Unsaturated fatty acids readily react with strong sulfuric acid with the introduction of either the sulfate group, $-OSO_2OH$, or the sulfonate group, $-SO_2OH$, at the double bond (see page 356) This reaction, followed by neutralization of the resulting sulfuric ester with sodium car-

[2] R S McKinney, N J Halbrook, and W G Rose, *Oil & Soap*, 19, 141–143 (1942)

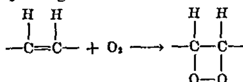
bonate, is carried out commercially to an extensive degree, in the preparation of so-called sulfonated oils for the textile industry, etc

(e) *Atmospheric Oxidation, Rancidity*

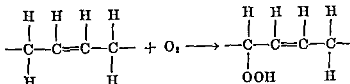
From a practical standpoint, atmospheric oxidation of fats may be more or less sharply differentiated into that occurring in highly unsaturated oils, which is accompanied by polymerization, and is generally useful, and that occurring in less unsaturated materials, which leads to the development of rancidity,[3] and is the source of most of the spoilage of edible fats and oils Oxidation of the former type is covered in a later chapter on paints and related products (pages 366–417) hence oxidation will be discussed here only in relation to rancidity

The development of rancidity, it should be noted, is not a phenomenon involving gross portions of the rancid fat According to the calculations of Pritzker and Jungkunz,[4] not more than 0 1% of the fat may actually decompose to form the volatile, low molecular weight compounds responsible for its rancid flavor and odor

The initial step in the oxidation of a fat is the addition of oxygen at or near the double bond of a fatty acid chain, to form unstable compounds which are generally designated as peroxides, the reaction according to classical fat chemistry being as follows



However, Farmer and co-workers[5] have demonstrated that, in the case unconjugated fatty acids oxidized at ordinary temperatures, the initial oxidation products consist of hydroperoxides, which are formed by the addition of oxygen at a carbon atom adjacent to the double bond and leave the latter intact



From comparative experiments conducted on methyl oleate at 20° and 120°C, Atherton and Hilditch[6] have concluded that the formation of

[3] For a comprehensive discussion of rancidity see the monograph of C H Lea *Rancidity in Edible Fats* Chem Pub Co, New York 1939

[4] J Pritzker and R Jungkunz *Z Untersuch Lebensm* **57**, 419–421 (1929)

[5] See for example E H Farmer, G F Bloomfield A Sundralingam and D A Sutton, *Rubber Chem Tech*, **15**, 756–764 (1942) and *Trans Faraday Soc*, **38**, 348–356 (1942), E H Farmer and D A Sutton *J Chem Soc*, **1943**, 119 122

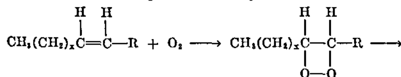
[6] D Atherton and T P Hilditch *J Chem Soc* **1944**, 105–108

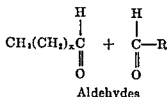
hydroperoxides predominates at the lower temperature, but that there is little formation of these compounds at the higher temperature

Whatever their structure, the peroxides, etc are but intermediate and transitory products in the general course of oxidation They are highly reactive, and quickly decompose or combine with one another in a variety of poorly understood reactions, to yield the compounds actually responsible for rancid flavors and odors They are estimated through their ability to liberate iodine from potassium iodide in glacial acetic acid solution The *peroxide value* of a fat is a measure of its content of reactive oxygen, in terms of millimoles of peroxide, or milliequivalents of oxygen, per 1000 grams of fat.

The position of the double bond has a considerable effect upon both the readiness with which oxygen is added, and the reactivity of the resultant peroxides If two or more double bonds are present in one fatty acid chain, they appear to have a mutually activating effect Thus, for example, linoleic acid, with two double bonds, oxidizes more easily, and forms more reactive products than does oleic acid, which has one double bond,[7] and the difference between the two is rather greater than can be explained simply by the difference between the number of double bonds in the two cases The mutually activating influence of the double bonds is particularly marked where the bonds are conjugated Thus elaeostearic acid oxidizes more readily than does linolenic acid[8] Fatty acids in the free form are generally inclined to oxidize more readily than when combined as glycerides, but some authorities, notably Lea,[3] believe this is probably due to injury of the acids during preparation Certainly the development of a moderate amount of free fatty acids in a sample does not affect its stability to any large degree

The typical sharp, unpleasant odor of rancidity is believed to be chiefly due to the presence of aldehydes of medium molecular weight, and particularly heptylic and nonoic aldehydes Such compounds may be formed by the oxidation and rupture of a fatty acid chain at a double bond





[7] G E Holm, G R Greenbank, and E F Duphur, *Ind Eng Chem*, **19**, 156–158 (1924)

[8] J E Meyers, J P Kass, and G O Burr, *Oil & Soap*, **18**, 107–109 (1941),

A great variety of other substances, including low molecular weight aldehydes and acids, hydroxy acids, keto acids, ketones, etc , are also found in rancid fats, but it is not believed that any of these contribute in any important way to the flavor or odor of these fats [9]

Except for the tests for peroxides, mentioned above, most of the chemical tests devised for the detection of rancidity or the estimation of its intensity depend upon the aldehyde content of the fat The *Kreis test*, which is qualitative or roughly quantitative, depends upon the presence of a specific class of compounds, namely acetals of epihydrin aldehyde The *Schiff test* is a qualitative test for aldehydes The quantitative methods of Issoglio and Kerr depend upon the presence of low molecular weight, steam-volatile aldehydes, whereas that of Schibsted is for aldehydes of high molecular weight The bisulfite method of Lea is particularly for the estimation of aldehydes of medium molecular weight

Although oleic acid oxidizes much less readily than the more unsaturated acids, and lard, hydrogenated shortenings, and similar products exhibit progressively improved stability as their ratio of oleic to more unsaturated acids increases, it is nevertheless probable that the odor and flavor of true rancidity is contributed largely or entirely by oleic acid The methyl and ethyl esters of oleic acid readily acquire a rancid odor with limited oxidation, whereas the esters of linoleic and linolenic acid develop relatively little odor after the absorption of large amounts of oxygen, and never develop an odor bearing much resemblance to that of truly rancid fats [10] The amount of oxygen required to produce rancidity will vary considerably according to the composition of the oil, the presence or absence of antioxidants, and the conditions under which oxidation is carried out, but will ordinarily amount to about 10% to 50% of the oil by volume, or 0 015% to 0 075% by weight. Fats high in oleic acid and low in linoleic acid will become rancid after the absorption of less oxygen than fats in which the ratio of these acids is reversed

The rate at which oxygen is absorbed by a fat is markedly accelerated by heat, and also by exposure to light, particularly in the ultraviolet and near-ultraviolet regions Hydrolysis does not necessarily, or even usually accompany the oxidation of a fat Consequently, the free fatty acid content of a fat is not, as is sometimes supposed, an indication of the presence or absence of rancidity

When the course of oxidation of a fat is followed experimentally, either by measuring the amount of oxygen absorbed, or determining the peroxide value of the fat, it will be found that the course of oxidation exhibits two distinct phases (see Fig 1) During the initial phase, oxidation proceeds at a relatively slow, and more or less uniform, rate Then, after a certain

[9] W C Powick, *J Agr Research*, **26**, 323-362 (1923)
[10] G E Holm and G R Greenbank, *Ind Eng Chem* , **16**, 518 (1924)

critical amount of oxidation has occurred, the reaction enters a second phase characterized by a rapidly accelerating rate of oxidation, and an eventual rate many times greater than that observed in the initial phase The point at which the sample begins to smell and taste rancid coincides with the beginning or the early part of the second phase The initial period of relatively slow oxidation of a fat is termed the induction period

There is a considerable difference among different fats in the manner in which their oxidation and accompanying flavor deterioration proceeds The more highly saturated animal fats and hydrogenated oils, whose unsaturated acids consist largely of oleic acid, are relatively little altered in flavor and odor during the early phases of oxidation The onset of rancidity in such fats is both sudden and definite On the other hand, rela-

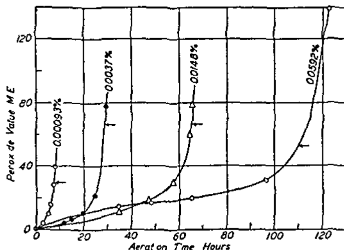


FIG 1 —Typical stability curves of fats aerated at 99°C Antioxidant free fat containing different amounts of antioxidant concentrates (tocopherols) from peanut oil Arrow indicates point at which sample smelled rancid [11]

tively unsaturated oils, such as natural cottonseed or soybean oils exhibit a more gradual deterioration in flavor and odor, and a greater tendency to develop unpleasant flavors and odors different from those of true rancidity In such oils it is often difficult to determine organoleptically just when rancidity actually begins Under test conditions which accelerate their rate of oxidation, the more unsaturated oils also absorb more oxygen and develop higher peroxide values before the end of the induction period, and the induction period is less clearly distinguishable from the later phase of oxidation

While the ease and rapidity with which an oil will oxidize depends primarily upon its content of reactive double bonds, it is also considerably

[11] A E Bailey G D Oliver W S Singleton and G S Fisher, *Oil & Soap*, 20, 251-255 (1943)

influenced by the presence of certain accessory substances, which may occur in the oil either naturally or adventitiously Those substances which favor the natural oxidation of fats are termed pro-oxidants, while those inhibiting oxidation are known as antioxidants or inhibitors For further discussion of antioxidants, see pages 29 *et seq*

All naturally occurring fats and oils contain characteristic antioxidants In vegetable oils these substances appear to serve the specific purpose of protecting the oil from deterioration during the normal life of the parent seed or fruit Vegetable oils normally have a larger content of antioxidants than do animal oils, hence are usually more stable than animal oils of an equivalent degree of unsaturation.

A remarkable characteristic of the antioxidants is their great effectiveness in low concentrations in the oil The natural antioxidant content of an oil may not amount to more than a few hundredths, or even thousandths, of one per cent

A mechanism by which traces of a foreign material are able to powerfully inhibit a reaction was first suggested by Christiansen,[12] and has since come to be generally accepted as the one governing the action of antioxidants According to this so called chain reaction theory, a molecule of fat and a molecule of oxygen are able to unite to form a peroxide only after one or the other, or both, are activated by the absorption of a quantum of energy This energy may be radiant energy, proceeding from heat or light applied to the oil, or chemical energy, derived from molecules of reactive substances in the oil which are at a high energy level After union has occurred and peroxide formation is completed, the activating energy may be released and made available for the activation of a new molecule or molecules, to form a new peroxide A chain of reactions is thus set up, and the initial absorption of a single unit of energy will result in the formation of a great number of peroxide molecules, unless the chain is broken by absorption of the activating energy in extraneous reactions

The antioxidants are presumed to be substances which are capable of absorbing the activating energy and thus preventing it from being transmitted to further molecules of the oil or in other words, which are cabable of breaking the reaction chain If the average chain is normally very long, it will be seen that the presence of even a very small amount of antioxidant may be sufficient to materially reduce its length, with a corresponding reduction in the rate of oxidation The antioxidant will of course be itself oxidized in the process of breaking the chain

While it does not appear to be definitely established that the presence of antioxidants is solely responsible for the induction period exhibited by all natural fats and oils, there can be little doubt that it is responsible to a large

[12] J A Christiansen, *J Phys Chem*, 28, 145–148 (1924)

degree Swift, Rose, and Jamieson[13] found that the carefully purified methyl esters of cottonseed oil had no induction period, and that, in tests of specimens of these esters which has been stabilized with added α-tocopherol, the end of the induction period coincided with the disappearance of the antioxidant, through oxidation However, the presence of tocopherols does not appear to insure a low rate of oxidation; Oliver, Singleton, and Bailey[14] have noted in some cases a considerable content of tocopherols at the end of the induction period of oxidizing fats Tocopherols attain

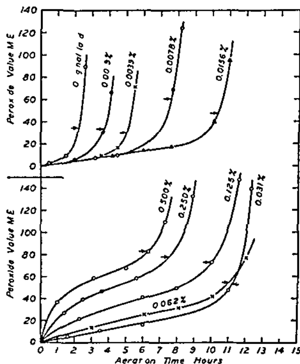


FIG 2—Effect on the stability of lard of adding different amounts antioxidants (calculated as tocopherols) from peanut oil Arrow indicates point at which sample smelled rancid [14]

their maximum effectiveness as antioxidants at comparatively low levels of concentration, roughly equivalent to their natural concentrations in vegetable oils [13, 14] Above the optimum concentration they are inclined to act as pro-oxidants (see Fig 2)

It is believed that pro-oxidants function principally through their catalytic effect on the oxidation of antioxidants Among the substances of known pro-oxidant activity which may sometimes be found in commercial fats and oils are soaps of various metals, formed through the action of free fatty acids upon tanks and other metallic equipment used in processing or storing

[13] C E Swift, W G Rose, and G S Jamieson, *Oil & Soap*, **19**, 176–180 (1942)
[14] G D Oliver, W S Singleton, and A E Bailey, *Oil & Soap* **21**, 188–193 (1944)

the oils Copper, in particular, is a very strong pro-oxidant,[15] being effective in a concentration of less than one part per million Copper and copper-bearing alloys are consequently avoided in the fabrication of equipment for handling edible fats and oils, the use even of brass valves or cocks is avoided in mills and refineries From a practical standpoint, the possible harm which a metal may do to the stability of oils depends both upon its pro-oxidant activity *per se*, and the extent to which it may become dissolved in the oil Materials high in free fatty acids are much more inclined to dissolve metals than are neutral oils In ordinary processing operations common carbon steel does not appear to be sufficiently corroded by oils to seriously affect their stability

The stability of fats is usually evaluated in the laboratory by subjecting samples to conditions which greatly accelerate their normal course of oxidation, and noting the time required for rancidity to develop In the *aeration test*, otherwise known as the *Swift stability test*,[15] samples are aerated at 97 7°C In a modification of this test,[16] the evaluation of stability is made even more rapid by conducting the aeration at 110°C The *Schaal test*[17] involves simple incubation of the sample in an oven at 60°C

(*f*) *Reactions of Hydroxyl Groups*

Hydroxyl groups may be introduced into fatty acid chains by various means, in the case of the castor oil, which contains ricinoleic acid, they are present naturally In industrial practice, the most important reaction involving the hydroxyl group is the dehydration of castor oil to produce a drying oil with conjugated acids This process is discussed on pages 696–697

Hydroxyl groups in fats are readily acetylated by reaction with acetyl chloride or acetic anhydride in the presence of pyridine, etc , this reaction constitutes the basis of various analytical methods for the estimation of these groups The *acetyl value* is defined as the number of milligrams of potassium hydroxide required to neutralize the acetic acid produced by hydrolysis of one gram of acetylated fat The *hydroxyl number* is the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram of fat Methods for the estimation of hydroxyl content do not differentiate between hydroxyl groups in the fatty acid chains and those present in mono or diglycerides, hence partially hydrolyzed fats may exhibit a considerable acetyl value without containing hydroxy acids

[15] A E King H L Roschen and W H Irwin *Oil & Soap* 10, 204 207 (1933)
[16] V C Mehlenbacher *Oil & Soap* 19, 137 139 (1942)
[17] N T Joyner and J E McIntyre *Oil & Soap* 15 184–186 (1938)

CHAPTER III

PHYSICAL PROPERTIES OF FATS AND FATTY ACIDS

1. Physical Structure of Fats and Fatty Acids

(a) *Structure in the Liquid Phase*

In the liquid form, fatty acids are known to be associated, *i e*, molecules of the acids are joined in pairs Association may occur not only between similar molecules, but also between molecules of different fatty acids It has often been observed that a fatty acid which is relatively insoluble in a given organic solvent may become more soluble in the presence of a second, relatively soluble acid[1] This effect is presumably occasioned by the formation of soluble compounds of the two acids In general, however, dissolving the acids in an organic solvent greatly reduces association

Association of glyceride molecules also occurs in liquid fats As in the case of the fatty acids, dissociation tends to occur in the presence of an organic solvent Not a great deal is known concerning compound formation in liquid glycerides, although it would appear that in this respect glycerides are in general similar to fatty acids

(b) *Structure in the Solid Phase*

The crystals of fatty acids are considered to be made up of units containing four molecules each[1a] The molecules are arranged in the form of two pairs, placed end to end, with the hydrocarbon chains in alignment, and carboxyl groups of the two in juxtaposition Thus the length of the cell is approximately twice that of each molecule, and the breadth and depth correspond to considerably lesser distance between the hydrocarbon chains

Glyceride molecules are believed by Malkin[2] to have the following con-

[1] See, for example, P Waentig and G Pescheck, *Z physik Chem*, **93**, 529–569 (1919)

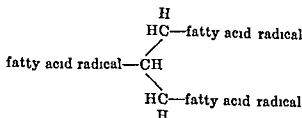
[1a] S B Hendricks, *Chem Revs*, **7**, 431–477 (1930)

[2] T Malkin, *Nature*, **127**, 126 (1931) C E Clarkson and T Malkin, *J. Chem Soc*, **1934**, 666–671

T Malkin and M L Meara, *ibid*, **1939**, 103–108 T Malkin and M G R Carter, *ibid*, **1939**, 577–581

T Malkin and M L Meara, *ibid*, **1939**, 1141–1144 M G R Carter and T Malkin, *ibid*, **1939**, 1518–1521

figuration, with the fatty acid radical in the β-position extending in an opposite direction from those in the α- and α′-positions



Crystals of glycerides appear to be made up of molecules joined as indicated in Figure 3, to produce unit cells which, like the fatty acid cells, have a length approximately twice that of the fatty acid chains In the

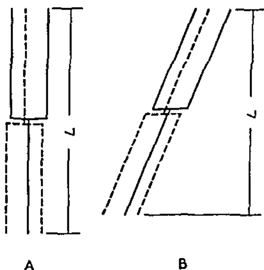


Fig 3 —Structure of triglyceride crystals (according to Malkin)

crystals of both fatty acids and glycerides, the unit cells are arranged in superimposed layers, with their long axes parallel, and the terminal CH_3 groups of the hydrocarbon chains forming the layer boundaries All present knowledge of the intimate structure of these and other crystals is derived from x-ray diffraction measurements,[3] which indicate the long spacings from end to end of the cells (L and L' of Fig 3), and the short spacings corresponding to distances between the hydrocarbon chains

Mixtures of both fatty acids and glycerides are inclined to form mixed crystals containing dissimilar molecules The work of Slagle and Ott[4]

[3] See the preceding references to the publications of Malkin and co workers, and also various publications of F Francis, S H Piper, A C Chibnall, *et al*, particularly the resume of data pertaining to the fatty acids by F Francis and S H Piper, *J Am Chem Soc*, 61, 577–581 (1939)

[4] F B Slagle and E Ott, *J Am Chem Soc*, 55, 4404–4418 (1933)

has shown that, in general, the saturated fatty acids form solid solutions rather than definite compounds Solid solution formation was observed in mixtures of fatty acids differing in chain length by as much as 8 carbon atoms The tendency to form mixed crystals is particularly marked in the case of adjacent members of the saturated fatty acid series Binary mixtures of such acids generally form two eutectics, with one corresponding to a nearly equimolecular mixture of the two acids, and the other containing about 28 mole per cent of the lower molecular weight acid [5] It has also been shown[6] that eutectics are formed in the systems stearic-oleic acid and palmitic-oleic acid, these contain respectively about 2 5% and 5% of the saturated acids Oleic acid forms eutectics with linoleic and linolenic acids[7], but no eutectic has been detected in the system linoleic-linolenic acid

The melting and solidification point curves of the system tristearin-tripalmitin[8] have the same general form as the corresponding curves for stearic and palmitic acids, hence the presence of eutectics in this system appears probable No attempt has been reported to characterize the crystals appearing in binary glyceride systems or in the multicomponent systems of natural plastic fats It would appear probable, however, that these, like crystals from fatty acid systems, are to be placed generally in the category of solid solutions, and hence are mixed and continuously variable in composition

Because of the high viscosities of fats and oils, the molecular orientation requisite for crystal formation occurs with relative slowness Consequently, these materials are greatly inclined to supercool, and after melting may remain for hours, and in some cases even days or months before crystallization will take place When crystals are once established in fats, the crystal nuclei are very persistent, and may remain, invisible, after the fat has been heated far above its apparent melting point This particular characteristic of fats and oils has many practical implications Thus, for example, after a sample of salad oil has become solidified, in the course of a cold test, it must be heated to a relatively high temperature before a second test is performed, otherwise the persistence of crystal nuclei will cause it to deposit crystals in an abnormally short time It is apparently due to the persistence of crystal nuclei that commercial shortenings, margarine, lard, and butter are enabled to retain their original smooth texture through

[5] See *for example*, F *Francis* F J E Collins and S H Piper, *Proc Roy Soc London* A158, 691–718 (1937), and H A Schuette and H A Vogel *Oil & Soap*, 16, 209–212 (1939)

[6] J C Smith, *J Chem Soc* 1939, 974–980

[7] H W Stewart and D H Wheeler, *Oil & Soap*, 18, 69 71 (1941)

[8] R B Joglekar and H E Watson *J Indian Inst Sci* , A13, 119–127 (1930)

the vicissitudes of temperature normally following their original solidification

The addition of even a small proportion of an organic solvent to an oil markedly reduces its viscosity, and enables it to deposit crystals with correspondingly greater readiness

Glycerides are polymorphous,[9] i e, capable of existence in multiple crystal forms, each of which has a distinctive melting point, density, latent heat, etc Simple triglycerides exist in three well defined forms, whereas most mixed glycerides are considered to have at least four forms In all cases, these materials are monotropic, i e, the transition from one form to another is irreversible, and can proceed only in the direction of producing crystal modifications of progressively higher melting point and greater thermodynamic stability

X-ray diffraction examinations[3] reveal a similar multiplicity of crystal forms in the saturated fatty acids However, transformations from one form to another occur so readily that multiple melting points are not observed Transformation is much less rapid in the triglycerides, and these will often exhibit multiple melting points when rapidly solidified and then heated somewhat rapidly

The polymorphism of tristearin is typical and therefore may be described in some detail The crystal form obtained when tristearin is solidified is dependent principally upon the rapidity with which the sample is chilled Very rapid chilling produces the form designated by Ferguson and Lutton[9] as the γ form, which melts at 54 5°C Less rapid chilling is inclined to produce the α form, melting at 65°C Very slow chilling conducive to maximum freedom in molecular orientation, will cause crystallization to take place in the most stable, or β form, which melts at 71 5°C From solvents the fat crystallizes only in the β form In a massive portion of solidified material, a mixture of the various forms will normally exist, due to relatively slow cooling, and unequal rates of cooling in different portions of the fat Transitions of the γ form to the α form, and of the α form to the β form occur at temperatures approaching in each case the melting point of the lower melting form However, at temperatures much below its melting point the transformation of an unstable form is so slow as to be virtually undetectible Both the density and the latent heat of the different forms increase progressively as the latter become higher melting and more stable

Mixtures of fully saturated triglycerides exhibit polymorphism comparable to that of single glycerides, and polymorphism is also evident in blends

[9] ... n fatty acids and fats see the ... et al and the review of the polymorphism in fats by R H Ferguson ... Chem Revs 29, 355-384 (1941)

of saturated glycerides with ordinary oils containing mixed unsaturated and saturated-unsaturated glycerides Polymorphism is also pronounced in certain relatively simple mixtures of glycerides containing virtually no fully saturated members, as for example in cocoa butter However, the obviously complex mixtures resulting from the partial hydrogenation of vegetable oils to produce shortenings, etc , are not ordinarily polymorphous, even when rapidly solidified

Polymorphism is caused by the glyceride molecules assuming different arrangements in the cell units The x-ray data of Malkin and co-workers furnish some evidence as to the probable cell structure in each of these forms In the case of tristearin, the γ-form has no characteristic long spacing, and but a single somewhat ill defined short spacing of 4 2° Å The molecular orientation existing in this form would therefore appear to be confined to a fair degree of alignment of the hydrocarbon chains, with no definite layer formation The α form has a long spacing of 50 6 Å, which corresponds to the length of two hydrocarbon chains, and hence indicates perpendicularity of the cells in the layers, as illustrated at *A* in Figure 3 There is a single but fairly sharp short spacing of 4 2 Å, which would indicate that the hydrocarbon chains are not in fixed positions with respect to their relative rotation about the chain axis The long spacing of the β-form is but 45 Å, which may be taken as evidence that the chain axis is tilted at an angle to the planes determined by the terminal CH_3 groups, as illustrated at *B* in Figure 3 There are sharply defined side spacings of 3 7, 3 9, 4 6, and 5 3 Å, which would indicate that the relative positions of the hydrocarbon chains are fixed [9a]

2. Oiliness and Viscosity

One of the most noticeable characteristics of oils and fats is their "oiliness," or ability to form lubricant films In this respect, they are quite similar to long chain hydrocarbons Although the fatty oils have been largely replaced by petroleum products as lubricants for machinery, there are a number of other technical applications in which their primary function is that of lubrication, and even in some edible products their lubricating action is important

Oils owe their relatively high viscosities to the long chain structure of their glyceride molecules, hence the viscosity of blown, heatbodied, or other

[9a] Very recent work carried out by the author and associates and by workers at the University of Pittsburgh and the Procter and Gamble laboratories indicates crystal structures in the simple saturated triglycerides somewhat different from those deduced by Malkin and co workers The lowest melting or γ form has been found to be actually crystalline rather than vitreous, and to have long and short spacings corresponding to those ascribed by Clarkson and Malkin to the α form A new crystal structure, with a long spacing only slightly different from that of the β form, and with two side spacings, has been found for the α form

of micelles or other aggregates to become oriented under high shearing stresses

The viscosity of oils is very markedly reduced by the addition of an organic solvent Viscosity data on mixtures of soybean oil with a commercial petroleum naphtha consisting largely of hexane (Skellysolve B) with ethylene dichloride, and with trichloroethylene have been published by Johnstone, Spoor, and Goss[13]

Fatty acids are slightly less viscous than the corresponding triglycerides Thus completely hydrogenated cottonseed oil has a viscosity of about 11 5 centipoises at 90°C ,[11] whereas the viscosities of palmitic and stearic acids at this temperature are, respectively, about 5 and 6 centipoises

TABLE 11
VISCOSITY OF FATS AND OILS*

Oil	Acid No	Sp gr, 20/4°C	Kinematic viscosity centistokes		Saybolt viscosity	
			100 F	210°F	100°F	210 F
Almond	2 85	0 9188	43 20	8 74	201	54 0
Olive	—	0 9158	46 68	9 09	216	55 2
Rapeseed	0 31	0 9114	50 64	10 32	234	59 4
Mustard	—	0 9237	45 13	9 46	209	56 9
Cottonseed	14 21	0 9187	38 88	8 39	181	52 7
Soybean	3 50	0 9228	28 49	7 60	134	50 1
Linseed	3 42	0 9297	29 60	7 33	139	49 2
Raw perilla	1 36	0 9297	25 24	6 85	120	47 6
Sunflower	2 76	0 9207	33 31	7 68	156	50 3
Castor	0 81	0 9619	293 4	20 08	1368	97 7
Coconut	0 01	0 9226	29 79	6 06	140	45 2
Palm kernel	9 0	0 9190	30 92	6 50	145	46 5
Lard	3 39	0 9138	44 41	8 81	206	54 2
Neatsfoot	13 35	0 9158	43 15	8 50	200	53 1
Sardine	0 57	0 9384	27 86	7 06	131	48 3
Cod liver	—	0 9138	32 79	7 80	153	50 7
Refined whale	0 73	0 9227	31 47	7 48	147	49 7
Sperm	0 80	0 8829	22 99	5 70	110	44 1

* According to A R Rescorla and F L Carnahan *Ind Eng Chem* 28 1212 1213 (1936)

3 Surface and Interfacial Tension and Other Surface Properties

Oleic acid has been reported to have a surface tension against air of 32 5 dynes per cm at 20°C , and an interfacial tension against water of 15 6 dynes per cm at the same temperature Corresponding surface and interfacial tensions reported for ricinoleic acid at 16°C are 35 8 and 14 3 dynes per cm and for caprylic acid at 18 1°C , 28 8 and 8 2 dynes per cm

Triolein is reported to have surface tensions (in dynes per cm) of 40 1 at 17°C , 29 3 at 99 8°C and 25 0 at 200 6°C The surface tension of cottonseed oil measured by the du Nuoy ring instrument at 45°C , is

[13] H F Johnstone I H Spoor and W H Goss *Ind Eng Chem* 32 832 835 (1940)

about 35 5 dynes per cm , and the interfacial tension against water is about 27 dynes per cm The interfacial tension of an oil is greatly lowered by the presence of mono- or diglycerides

Neutral glycerides are relatively lacking in surface activity, and are in general much less inclined to be adsorbed at solid surfaces than the various nonoil constituents of natural fats and oils This circumstance is taken advantage of in ordinary bleaching of fats and oils by adsorption, and in the various adsorptive methods for the concentration of carotenoids, tocopherols, and phosphatides from oils Recently, however, it has been shown that the surface-active properties of glycerides and methyl esters as well as fatty acids are such that mixtures of these materials may be resolved by chromatography [14]

4. Density and Expansibility

The density of oils is in general greater the higher their degree of unsaturation, and the lower the molecular weight of their fatty acids However, the differences in density between individual oils is not large Hydrogenation of cottonseed oil corresponding to a reduction in iodine value of 100 units suffices to lower the density of the oil about 0 015, *e g* , from 0 895 to 0 880 at 60°C (140°F), or from 0 805 to 0 790 at 200°C (392°F.) The density of coconut oil, with an iodine value of about 9, is about the same as that of cottonseed, with an iodine value of 108, owing to the low average molecular weight of the acids in the former

The following expression was developed by Lund[14a] for the specific gravity, 15°/15° C , of liquid oils specific gravity = 0 8475 + 0 00030 (saponification value) + 0 00014 (iodine value)

Over the range of temperatures to which oils are ordinarily heated in processing, *i e* , about 50° to 500°F , the density exhibits a substantially linear variation with temperature, decreasing approximately 0 00064 for each increment in temperature of 1°C , or about 0 000355 for each 1°F [11] For pure tricaprin, trilaurin, trimyristin, tripalmitin, and tristearin, Joglekar and Watson[8] give the respective values of 0 00073, 0 00071, 0 00069, 0 00067, and 0 00067 per degree C The expansibilities of the saturated fatty acids are virtually identical with those of the corresponding triglycerides Garner and Ryder[14b] give coefficients of 0 00079, 0 00073, and 0 00072, respectively, for caprylic, capric, and lauric acids

At a given temperature, glycerides are considerably more dense in the solid state than in the liquid state Because of the fact that "solidified"

[14] See, for example, F T Walker and M R Mills, *J Soc Chem Ind* , **61**, 125–128 (1942), M M Graff and E L Skau *Ind Eng Chem* , *Anal Ed* , **15**, 340–341 (1943), and C E Swift, W G Rose, and G S Jamieson, *Oil & Soap*, **20**, 249–250 (1943)

[14a] J Lund, *Z Untersuch Nahru Genussm* , **44**, 113–187 (1922)

[14b] W E Garner and E A Ryder, *J Chem Soc* , **127**, 720–730 (1925)

fats commonly consist of a mixture of solids and liquid, in indeterminate proportions, the density of such fats is ordinarily of little significance However, dilatometric measures, of volume change as a function of temperature, through the melting range, are useful in phase investigations of fats Such measurements may be made very accurately, hence they constitute a sensitive means of indicating phase transformations, either from solid to liquid, or from one polymorphic form to another The dilatometric curves of fats, of expansion plotted against temperature, are composed of a succession of substantially linear sections separated by abrupt transition points The transition points obviously indicate the position of boundaries in the complex and as yet unexplored phase diagrams of these materials Representative curves (for lard and butterfat), according to Kraemer and Bailey,[15] are shown in Figure 5

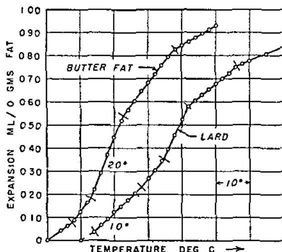


FIG 5 —Typical dilatometric curves of fats [15]

The densities of solid C_{12} to C_{18} saturated fatty acids and triglycerides in the most stable modification vary from about 1 02 to 1 04 at 0°C , with the members of lower molecular weight having the higher densities The coefficients of expansion of these substances in the solid form are of the order of 0 0002 per degree C

Relatively little data are as yet available on the volume changes associated with melting and solidification, or with polymorphic transformations in fats According to the data of Duffy, as quoted by Ferguson and Lutton,[9] tristearin expands 7 5% in transition from the most dense solid form to the liquid form The different volume changes are listed in detail as follows liquid to γ-form, 4 4%, γ-form to α form, 2 3%, α-form to β-form, 0 8% However, more recent experiments of Bailey and co workers

[15] E A Kraemer and A E Bailey, *Oil & Soap*, **21**, 254–256 (1944)

indicate a total volume change of 14% to 16% for C_{12} to C_{18} saturated triglycerides

The following values were reported by Dorinson, McCorkle, and Ralston,[17] and Joglekar and Watson[8] for the respective densities of the saturated fatty acids and their triglycerides at 80°C

	Acid	Glyceride
Caproic	0 8751	—
Caprylic	0 8615	—
Capric	0 8531	0 9059 (at 60°)
Lauric	0 8477	0 8943 (at 60°)
Myristic	0 8439	0 8860 (at 60°)
Palmitic	0 8414	0 8663
Stearic	0 8390	0 8632

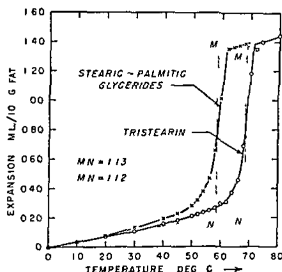


Fig 6 —Expansion during melting of tristearin and a fat containing stearic and palmitic acids interesterified in equi molar proportions [16]

The higher saturated fatty acids expand about 14% in melting

The density of mixtures of soybean oil with petroleum naphtha, ethylene dichloride, and trichloroethylene have been recorded by Johnstone, Spoor, and Goss [13]

5. Thermal Properties

(a) *Melting and Solidifying Points*

The melting point of a material is actually the temperature at which there is an equilibrium between the solid and liquid phases Elaborate methods are required for precisely determining the true melting point, but a close approximation is obtained by the ordinary technique of slowly heating the sample in a capillary tube, and noting the point at which all

[16] A E Bailey and E. A Kraemer, *Oil & Soap*, **21**, 251-253 (1944)

[17] A Dorinson M R. McCorkle, and A W Ralston *J Am Chem Soc*, **64**, 2739-2741 (1942)

crystals disappear Single fatty acids or glycerides melt sharply, as do mixtures of highly saturated glycerides However, natural fats and partially hydrogenated oils generally melt so gradually as to make a satisfactory determination of the melting point or more properly, the point of final melting, by this method impossible A number of empirical methods are in vogue, which in effect determine the temperature at which the sample becomes softened to an arbitrary degree These include the *slipping point, softening point, shot melting point* (point at which a small lead shot will drop through the sample), *incipient melting point*, etc The true temperature at which all crystals disappear from a plastic fat is best determined by dilatometric or calorimetric methods

The melting points of a number of fatty acids and glycerides[18,19] are recorded in Tables 12, 13 and 14 The data recorded in these tables illustrate the following general principles underlying the melting behavior of glycerides

(*a*) Fatty acids are higher in melting point as their chain length and degree of saturation increase, and the melting points of the fatty acids are reflected in a general way in the melting points of the glycerides

(*b*) Simple triglycerides of the higher saturated fatty acids have slightly higher melting points than the acids, but the glycerides of the unsaturated acids melt slightly lower than the acids

(*c*) Mixed triglycerides containing two different fatty acids generally have melting points intermediate between the melting points of the simple

[18] Data on the simple saturated glycerides are from C E Clarkson and T Malkin, *J Chem Soc* **1934**, 666–671 Those on triolein and trilinolein are from D H Wheeler, R W Riemenschneider, and C E Sando, *J Biol Chem*, **132**, 687–699 (1940) Those on trielaidin and trierucin are from M G R Carter and T Malkin, as reported by M L Meara in T P Hilditch *Chemical Constitution of Natural Fats*, Wiley, New York, 1941, p 358 Those on trilinolenin are from B F Daubert and A R Baldwin *J Am Chem Soc* **66**, 997–1000 (1944)

[19] The data on the mixed saturated glycerides are from the following publications H P Averill, J N Roche, and C G King, *J Am Chem Soc*, **51**, 866–872 (1929) and **52**, 365–367 (1930), H E Robinson, J N Roche, and C G King *ibid*, **54**, 705–710 (1932), B F Stimmel and C G King, *ibid*, **56**, 1724–1725 (1934), B F Daubert and C G King, *ibid*, **61**, 3328–3330 (1939), T Malkin and M R el Shurbagy, *J Chem Soc*, **1936**, 1628–1634, T Malkin, M R el Shurbagy, and M L Meara, *ibid*, **1937**, 1409–1413, T Malkin and M L Meara *ibid*, **1939**, 103–108, 1141–1144, and M G R Carter and T Malkin *ibid*, **1939**, 577–581, 1518–1521 Where two groups of authors have reported widely divergent melting points for the same glyceride, the [illegible]

[illegible] Daubert and A R Baldwin, *ibid*, **66**, 997–1000 (1944)

glycerides of the same acids However, in some cases, *e g*, the capric-oleic acid glycerides, the mixed glycerides are lower melting than the simple triglyceride of the lower melting acid

(*d*) Symmetrical glycerides containing two different fatty acids are higher in melting point than the corresponding unsymmetrical glycerides, and symmetrical diglycerides are higher melting than unsymmetrical diglycerides However, symmetrical *monoglycerides* are lower melting than the corresponding unsymmetrical monoglycerides

TABLE 12

MELTING POINTS OF THE COMMON FATTY ACIDS IN DEGREES C

Fatty acid	Low melting form	High melting form
Butyric	—	−8
Caproic	—	−1
Caprylic	—	16
Capric	—	31 3
Lauric	—	43 5
Myristic	—	54 4
Palmitic	—	62 9
Stearic	—	69 6
Oleic	13	16
Elaidic	—	44
Ricinoleic	—	5
Erucic	—	34
Linoleic	—	−7
Linolenic	—	−13

TABLE 13

MELTING POINTS OF DIFFERENT FORMS OF SIMPLE TRIGLYCERIDES IN DEGREES C

Triglyceride	γ form	α form	β form
Tricaprin	−15	18 0	31 5
Trilaurin	15	35 0	46 4
Trimyristin	33	46 5	57 0
Tripalmitin	45	56 0	65 5
Tristearin	54 5	65 0	71 5
Triolein	−32	−12	5 0
Trielaidin	15 5	37 0	41 5
Trierucin	6	25	32 5
Trilinolein	—	−43	−13 1

(*e*) Diglycerides are higher in melting point than the corresponding simple triglycerides, and monoglycerides are in turn higher melting than the diglycerides

Two analytical methods in common use depend upon the solidifying points of fats and fatty acids Neither represents a condition of equilibrium between the solid and liquid phases, on the contrary, they simply record the maximum temperature to which the fat is carried by heat of crystallization, when a sample of given size is solidified under specified conditions The solidifying point of the mixed fatty acids of a fat, so

determined, is known as the *titer*. The solidifying point of the glycerides is termed the *setting point*, or *congeal point*.

TABLE 14

M = myri[illegible]
acid, ll =

Glyceride	M p , °C
Monoglycerides	
A-OH -OH	19 4
C-OH—OH	53 0
OH—C—OH	40 4
L-OH—OH	63 0
OH—L—OH	51 1
M-OH—OH	70 5
OH—M—OH	61 0
P-OH—OH	77 0
OH—P—OH	68 5
S OH—OH	81 5
OH—S—OH	74.4
o—OH—OH	35 2
l-OH—OH	15 0
ll-OH—OH	17 0
e-OH—OH	58 5
Diglycerides	
C-OH—C	44 5
L-OH—L	56 5
M OH—M	65 5
P-OH-P	72 5
S OH—S	78 0
L-OH—S	62 0
M OH—S	66 0
P-OH—S	71 0
L-OH-o	32 0
M-OH-o	41 0
P-OH-o	46 0
S-OH-o	54 0
Mixed saturated triglycerides	
B-B-S	32 0

Glyceride	M p , °C
C-C-L	30 0
C-L-C	37.5
C-C-M	34 5
C-M-C	34 0
C-C-P	35 0
C-P-C	40 0
C-C-S	41 0
C-S-C	44 5
L-L-C	35 5
L-C-L	38.5
L-L-M	43 5
L-M-L	48 0
L-L-P	46 5
L-P-L	47 8
L-L-S	45 0
L-S-L	47 0
M-M C	43 5
M-C-M	43 5
M M-L	46 5
M-L-M	50 0
M M-P	54 0
M-P-M	58 5
M-M-S	56 0
M-S-M	55 5
P-P-C	45 5
P-C-P	51 5
P-P-L	54 0
P-L-P	53 5
P-P-M	57 0
P-M-P	60 0
P-P-S	62 5
P-S-P	68 0
S S A	42.7
S-A-S	47.2

Glyceride	M p , °C
S-S-B	47.6
S-B-S	51.8
S-S-C	49 0
S-C-S	57.0
S-S-L	52.0
S-L-S	60 5
S-S-M	58 5
S-M-S	62 5
S-S-P	65 0
S-P-S	68.0
Mixed unsaturated triglycerides	
o-o-A	−10 0
o o-B	−5 6
o-o-C	0 5
o o-L	6 5
o-o-M	13.5
o-o-P	19.[illegible]
o-o-S	23 [illegible]
o-C C	4.0
C-o-C	6.0
o-L-L	20 0
L-o-L	15 0
o-M-M	25 0
M-o-M	27 0
o-P-P	34.5
P-o P	36 0
o-S-S	38 5
S-o S	43 0
e e C	25.0
e e-L	35 5
e-e-M	40 0
e-B-B	3 0
e-C C	15.0
e-L-L	27.0
e-M-M	39 5

(b) *Heats of Combustion*

The heats of combustion of the saturated fatty acids increase with increase in the chain lengths of the acids, and vary from about 5900 cal per g for butyric acid to about 8900 for lauric, 9600 for stearic, and 9800 for behenic Values for the unsaturated acids are slightly lower than for saturated acids of the same chain length, about 9450 beihg recorded for oleic acid, and 9350 for linoleic acid Triglycerides have substantially the same heats of combustion as the fatty acids of which they are composed, hence the heat of combustion of common fats, such as lard and tallow, is about 9500 cal per g [20] All the preceding values are expressed in terms of constant volume at 15°C

(c) *Heat Capacity and Latent Heats*

Garner and co workers[21] have furnished complete data on the heats of crystallization and specific heats of all the common saturated fatty acids

TABLE 15
LATENT HEATS AND HEAT CAPACITIES OF SATURATED FATTY ACIDS[a]

Acid	Latent heat cal /g	Specific heats cal /g	
		Solid	Liquid
Caproic	31 0	0 4495 (−33 to −10°C)	0 5105 (0 to 23°C)
Caprylic	35 4	0 4650 (0 to 12°)	0 5050 (18 to 46°)
Capric	38 8	0 5009 (0 to 24°)	0 4989 (35 to 65°)
Lauric	43 8	0 5116 (19 to 39°)	0 5146 (48 to 78°)
Myristic	47 1	0 5209 (24 to 43°)	0 5157 (to 84°)
Palmitic	50 7	0 4920 (22 to 53°)	0 5416 (to 68°)
Arachidic	54 3	0 4597 (20 to 56°)	0 5663 (to 100°)
Behenic	55 1	0 4854 (18 to 71°)	0 5556 (to 109°)
Lignoceric	57 3	0 4656 (18 to 78°)	0 5855 (to 109°)

[a] According to W E Garner, F C Madden, and J E Rushbrooke, *J Chem Soc*, 1926, 2491–2502, W E Garner and F C Randall, *ibid*, 1924, 881–896, and W E Garner and A M King, *ibid*, 1929, 1849–1861

except stearic acid Their work included determinations of the specific heats of both solid and liquid phases near the melting points of the acids Their data are summarized in Table 15

Relatively little is known concerning the heat capacities and latent heats of triglycerides or of commercial fats and oils The work of Oliver, *et al* [22] in which cottonseed oil and hydrogenated cottonseed oil were examined calorimetrically over the temperature range of −100° to 65°C, furnishes

[20] See for example, F W Krzywanek *Biochem Z*, 159, 507–509 (1925)

[21] W E Garner F C Madden, and J E Rushbrooke, *J Chem Soc*, 1926, 2491–2502 W E Garner and F C Randall, *ibid*, 1924, 881–896, and W E Garner and A M King, *ibid*, 1929, 1849–1861

[22] G D Oliver, W S Singleton, S S Todd, and A E Bailey, *Oil & Soap*, 21, 297-300 (1944)

virtually the only complete data of reasonably high accuracy Over the range of temperatures covered the specific heat, C_p of the completely solid and completely liquid oils could be expressed in terms of the temperature in degrees C, t by the following equations

For the solid oil
$$C_p = 0.442 + 0.00172\ t$$
For the solid hydrogenated oil
$$C_p = 0.407 + 0.00158\ t$$
For the liquid oil
$$C_p = 0.462 + 0.00061\ t$$
For the liquid hydrogenated oil
$$C_p = 0.475 + 0.00055\ t$$

The heats of fusion of the unhydrogenated and hydrogenated oils were calculated to be 20 6 and 27 4 cal per g, respectively The hydrogenated

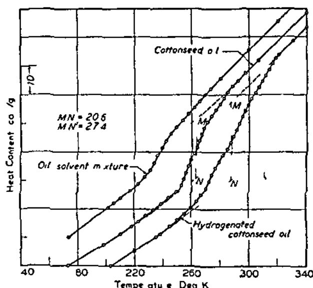


FIG 7 —Heat content *vs* temperature of cottonseed oil hydrogenated cotton seed oil (I V = 59 5) and a mixture of 52 1 parts cottonseed oil and 47 9 parts by weight petroleum naphtha (Skellysolve B) [22]

oil employed in this investigation had an iodine value of 59 5 and a consistency closely approximating that of commercial shortenings or margarines The data of these workers are shown graphically in Figure 7

Later work of the latter group of workers established the following equations for the heat capacity of highly hydrogenated cottonseed oil (iodine value = 0 85)

For the completely solid oil (−80° to −10°C)
$$C_p = 0.364 + 0.00135\ t$$
For the completely liquid oil (60° to 80°C)
$$C_p = 0.453 + 0.00097\ t$$

The heat of fusion of the oil was determined to be 44 3 cal per g The thermal data given here applied to the oil in its highest melting, most stable polymorphic form

By a different technique from that employed by Oliver *et al*, Gudheim[22a] found values ranging from about 45 to 52 cal per g for the heat of fusion of highly hydrogenated vegetable oils Rao and Jatkar[23] estimated the heats of fusion of tristearin in the β- and γ-forms to be 61 6 and 44 2 cal per g, respectively These values, however, appear to be too high Late work of the author and associates indicates respective values in the neighborhood of 54 and 39 cal per g, with a heat of transition, γ form to β form,

TABLE 16

SPECIFIC HEATS OF DRYING OILS AT HIGH TEMPERATURES[a]

Refined linseed oil		Soybean oil		Tung oil	
Temperature °F	Specific heat	Temperature °F	Specific heat	Temperature °F	Specific heat
167	0 504	167	0 568	156 2	0 516
192 2	0 499	185	0 579	158	0 510
192 2	0 474	266	0 582	174 2	0 516
203	0 502	284	0 591	185	0 534
208 4	0 504	284	0 606	195 8	0 528
215 6	0 493	303 8	0 589	208 4	0 542
249 8	0 498	318 2	0 596	208 4	0 546
287 6	0 513	321 8	0 597	264 2	0 595
305 6	0 540	339 8	0 603	275	0 596
323 6	0 539	357 8	0 623	294 8	0 630
341 6	0 563	374 0	0 640	311	0 644
374	0 605	379 4	0 630		
392	0 627	428 0	0 618		
426 2	0 664	446	0 655		
491	0 663	464	0 681		
528 8	0 680	482	0 698		
554	0 665	536	0 759		
		548 6	0 765		

[a] According to J S Long, J B Reynolds, and J Napravnik, *Ind Eng Chem*, **26**, 864–868 (1934)

at the γ-melting point, of *ca* 14 cal per g From heat of solution data, Rao and Jatkar estimated the heat of transition to be 15 6 cal per g

The specific heats of raw linseed oil, refined linseed oil, soybean oil, tung oil, and oleic acid were determined over large temperature ranges, but not with high accuracy, by Long, Reynolds, and Napravnik [24] Selected values from the data of these workers are presented in Table 16

[22a] A R Gudheim, *Oil & Soap*, **21**, 129–133 (1944)

[23] M M R Rao and S K K Jatkar, *J Indian Chem Soc*, **12**, 574–581 (1935)

[24] J S Long, J B Reynolds, and J Napravnik, *Ind Eng Chem*, **26**, 864–868 (1934)

The following values are given by Lederer[25] for the specific heats of some of the fatty acids at high temperatures

At	Stearic	Lauric	Oleic
10°C	—	—	0 462
50°C	—	0 513	0 489
100°C	—	0 543	0 549
150°C	0 585	0 596	0 638
200°C	0 660	0 674	—
250°C	0 775	0 776	—

TABLE 17
BOILING POINTS OF THE SATURATED ACIDS[a]

Pressure mm	Boiling point °C						
	Caproic	Caprylic	Capric	Lauric	Myristic	Palmitic	Stearic
1	61 7	87 5	110 3	130 2	149 2	167 4	183 6
2	71 9	97 9	121 1	141 8	161 1	179 0	195 9
4	82 8	109 1	132 7	154 1	173 9	192 2	209 2
8	94 6	121 3	145 5	167 4	187 6	206 1	224 1
16	107 3	134 6	159 4	181 8	202 4	221 5	240 0
32	120 8	149 2	174 6	197 4	218 3	238 4	257 1
64	136 0	165 3	191 3	214 6	236 3	257 1	276 8
128	152 5	183 3	209 8	234 3	257 3	278 7	299 7
256	171 5	203 0	230 6	256 6	281 5	303 6	324 8
512	192 5	225 6	254 9	282 5	309 0	332 6[b]	355 2[b]
760	205 8	239 7	270 0	298 9	326 2[b]	351 5[b]	376 1[b]

[a] W O Pool and A W Ralston, *Ind Eng Chem*, **34**, 1104–1105 (1942)
[b] Values obtained by extrapolation

(d) *Heats of Vaporization and Vapor Pressures*

Lederer[26] has calculated from vapor pressure data the following for the heats of vaporization of certain acids at atmospheric pressure.

	Cal /g		Cal /g
Capric	85	Palmitic	58 5
Lauric	68 5	Stearic	56
Myristic	*67 5*	*Oleic*	*57*

At 100 mm pressure, the above values are about 20% higher, at 5 mm. pressure, they are about 40% higher. Mills and Daniels,[27] from commercial plant operational data at 430–440°F, calculated the heat of vaporization of grease fatty acids to be 107–109 Btu per lb, and of red oil (commercial oleic acid) to be 124 Btu per lb

Complete data on the vapor pressures or boiling points of saturated acids containing from 6 to 18 carbon atoms as reported by Pool and Ralston[28] are recorded in Table 17 For the vapor pressures of fatty acids with

[25] E L Lederer, *Allgem Oel- u Fett Ztg*, **27**, 237 (1930)
[26] E L Lederer, *Seifensieder Ztg*, **57**, 67–71 (1930)
[27] V Mills and R C Daniels, *Ind Eng Chem*, **26**, 248–250 (1934)
[28] W O Pool and A W Ralston, *Ind Eng Chem*, **34**, 1104–1105 (1942)

more than 18 carbon atoms, see page 658. The boiling points (Table 17) of unsaturated acids appear to be very slightly (perhaps 2-3°C.) lower than those of saturated acids with the same number of carbon atoms; a partial separation of methyl oleate and methyl stearate in a mixture of the two has been reported[29] by the use of a very efficient laboratory column.

The vapor pressures of the glycerides, which are very much lower than those of the fatty acids, are not known with accuracy. Lederer[26] has estimated the vapor pressures of coconut oil and peanut oil as given in Table 18. From data obtained during the steam deodorization of hydrogenated cottonseed oil, Bailey[30] has estimated the vapor pressure of this fat to be approximately 0.04 mm. at 250°C. (482°F.).

TABLE 18
VAPOR PRESSURES OF COCONUT OIL AND PEANUT OIL[a]

Oil	Temperature		Vapor pressure, mm
	°C	°F	
Coconut	202	396	0.054
	227	441	0 16
	250	482	0 37
Peanut	227	441	0 0045
	250	482	0.010
	270	518	0 020

[a] As estimated by E L. Lederer, *Seifensieder Ztg* , 57, 67-71 (1930)

(e) Heats of Mixing

Mixing an organic solvent with an oil usually causes dissociation of the molecules of the latter, with a consequent absorption of heat. However, certain solvents, including particularly the chlorinated ones, cause little dissociation, and appear to form solvated compounds with the oil, so that the net effect of mixing is an evolution of heat. Among the solvents which bring about dissociation, the polar compounds have the most pronounced effect. Johnstone, Spoor, and Goss[13] reported the following changes in temperature upon mixing equal volumes of soybean oil and various solvents at 25°C.:

Hexane (Skellysolve B)	−0 86°C
Ethylene chloride, $C_2H_4Cl_2$	−1.44
Ethylene trichloride, CHCl CCl_2	+1 72
Ethyl alcohol, C_2H_5OH	−1.28
Chloroform, $CHCl_3$..	+3.61
Carbon tetrachloride, CCl_4	+0 44
Acetone, $(CH_3)_2CO$	−3 00
Benzene, C_6H_6	−0 67
Ethylene tetrachloride, $CCl_2.CCl_2$	+0 22
Phenylacetylene, C_6H_5:CH	+0 89

[29] A. W. Weitkampf and L C. Brunstrun, *Oil & Soap*, 18, 47-50 (1941)
[30] A E Bailey, *Ind Eng. Chem* , 33, 404-408 (1941).

Rough experiments carried out by Skau[31] indicate that petroleum naphtha (Skellysolve B) and cottonseed oil mixed at 25°C have a maximum

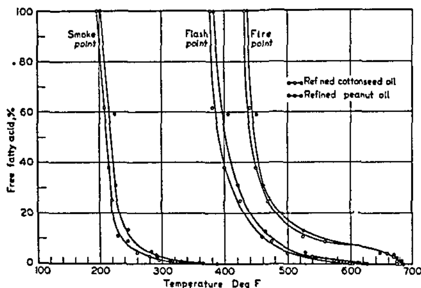


FIG 8 —Free fatty acids content *vs* smoke, fire, and flash points, cottonseed and peanut oils [32]

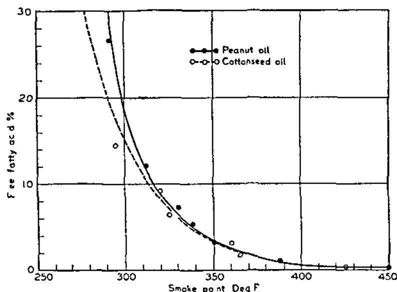


FIG 9 —Effect of small concentrations of free fatty acids on the smoke points of cottonseed and peanut oils [32]

negative heat of solution of the order of 2 cal per g of mixture, the maximum heat effect occurring with a mixture of about 60 weight per cent or

[31] E L Skau, *private communication* (1944)
[32] D A Morgan, *Oil & Soap* 19, 193-198 (1942)

12 mole per cent of oil, and corresponding to about 3 5 cal per g on the basis of the oil

(f) Smoke, Fire, and Flash Points

The smoke, fire, and flash points of a fatty material are measures of its thermal stability when heated in contact with the air The smoke point is the temperature at which decomposition products are evolved in sufficient quantity for them to become visible, the flash point is the temperature at which these products are evolved at such a rate that they are capable of being ignited but not of supporting combustion, and the fire point is the temperature at which they will support continued combustion

Fatty acids are much less stable than glycerides, hence the smoke, fire and flash points of ordinary oils are dependent principally upon their content of free fatty acids The smoke point of an oil such as cottonseed oil or peanut oil varies from about 450°F at a free fatty acid content of 0 01% to about 200°F at a free acid content of 100% Flash points of these oils exhibit a corresponding variation of from about 625° to 380°F and the variation of the fire point is from about 685° to 430°F Detailed data for these two oils are shown in Figures 8 and 9, taken from the publication of Morgan [32]

The degree of unsaturation of an oil has little, if any effect upon its smoke, fire, or flash points However, coconut oil or other oils containing acids of low molecular weight, have lower smoke, fire, and flash points than ordinary oils of equivalent free fatty acid content

6 Solubilities

(a) Mutual Solubilities of Fats and Fatty Acids with Water

The solubility of water in a number of the saturated fatty acids has been determined by Hoerr, Pool, and Ralston [33] Over the range of temperatures covered, there was in each case a linear relationship between the temperature and the percent water dissolved The solubility data are given in detail in Table 19 At high temperatures and pressures both fats and fatty acids dissolve large amounts of water According to the data of Mills,[34] at 450°F 100 parts of tallow fatty acids dissolves 9 parts of water, and 100 parts of coconut oil fatty acids dissolves 20 parts of water At high temperatures water is said to be slightly less soluble in neutral fats than in fatty acids The rapidity with which fats hydrolyze at high temperatures of course precludes the accurate determination of the solubility in a neutral fat

Hoerr *et al* also determined the effect of dissolved water on the solidification points of the fatty acids In a typical experiment, lauric acid

[33] C W Hoerr W O Pool and A W Ralston *Oil & Soap* **19** 126–128 (1942)
[34] V Mills (to Procter & Gamble Co), U S Pat 2 156 863 (1939)

containing 2 88% water was observed to have a solidification point 1 14°C below that of the pure acid

The solubility of water in winterized cottonseed oil at ordinary temperatures was determined by Parsons and Holmberg [35] The water dissolved amounted to 0 071% at 30°F and 0 141% at 90°F, with a linear

TABLE 19

SOLUBILITY OF WATER IN FATTY ACIDS[a]

Fatty acid	Temperature °C	Per cent water dissolved
Caproic	−5 4	2 21
	12 3	4 73
	31 7	7 57
	46 3	9 70
Heptylic	−8 3	2 98
	42 5	8 98
Caprylic	14 4	3 88
Nonylic	10 5	3 45
Capric	29 4	3 12
Undecylic	26 8	2 72
	57 5	4 21
Lauric	42 7	2 35
	75 0	2 70
	90 5	2 85
Tridecylic	40 8	2 00
Myristic	53 2	1 70
Pentadecylic	51 8	1 46
	90 0	1 62
Palmitic	61 8	1 25
Heptadecylic	60 4	1 06
Stearic	68 7	0 92
	92 4	1 02

[a] According to C W Hoerr, W O Pool, and A W Ralston, *Oil & Soap*, **19**, 126–128 (1942)

TABLE 20

SOLUBILITIES OF THE SATURATED FATTY ACIDS IN WATER[a]

Fatty acid	Grams acid per 100 grams water at temperature in degrees C				
	0 0°	20 0°	30 0°	45 0°	60 0°
Caproic	0 864	0 968	1 019	1 095	1 171
Caprylic	0 044	0 068	0 079	0 095	0 113
Capric	0 0095	0 015	0 018	0 023	0 027
Lauric	0 0037	0 0055	0 0063	0 0075	0 0087
Myristic	0 0013	0 0020	0 0024	0 0029	0 0034
Palmitic	0 00046	0 00072	0 00083	0 0010	0 0012
Stearic	0 00018	0 00029	0 00034	0 00042	0 00050

[a] A W Ralston and C W Hoerr, *J Org Chem*, **7**, 546–555 (1942)

relationship obtaining between temperature and water dissolved at intermediate temperatures

Ralston and Hoerr[36] have measured the solubility of the common saturated acids in water at temperatures between 0° and 60°C Selected portions of their data are recorded in Table 20

[35] L B Parsons and C O Holmberg, *Oil & Soap* **14**, 239–241 (1937)

[36] A W Ralston and C W Hoerr, *J Org Chem*, **7**, 546–555 (1942)

(b) *Solubility of Fats and Fatty Acids in Organic Solvents*

At temperatures above their melting points, both fats and fatty acids are freely miscible with a wide variety of hydrocarbons, esters, ethers, ketones, etc Incomplete miscibility with an organic liquid is, in fact, exceptional Out of 250 solvents tested by Bills[37] with coconut oil, cod liver oil, linseed oil, olive oil, and butterfat, there were but 28 which were not completely miscible with all five fats when mingled in equal proportions by volume, at room temperature

Below their melting points, fats and fatty acids become less soluble in organic solvents, and at temperatures approaching that of Dry Ice (−78°C), all fats, and all but the most highly unsaturated fatty acids, are but very slightly soluble

From a practical standpoint, the solubility of a single pure fatty acid or glyceride is seldom of much consequence In most operations in which the solubilities of fatty materials must be considered, the object is to obtain a maximum degree of separation in a mixture of compounds, through the differential solubility of the component members In such cases the solubility *per se* of the individual fatty acids or glycerides is of rather less importance than the degree to which the solvent permits association between different individuals The attainable degree of separation between a relatively high melting member, *A*, such as a saturated fatty acid, and a relatively low melting member, *B*, such as an unsaturated fatty acid, is not generally limited merely by the slight solubility of pure *A* at the lowest temperature at which pure *B* is still completely soluble Almost invariably, the factors actually responsible for making the separation somewhat less than complete are the tendency for *B* to leave the solution with *A*, in the form of mixed crystals, and the corresponding tendency of *A* to remain in the solution with *B*, in the form of relatively soluble *A B* complexes

Different solvents differ markedly in the degree to which they permit compound formation in solution, or more properly, in the degree to which they dissociate the naturally associated molecules in the liquid fat or fatty acids Among the earliest workers investigating the phenomenon of compound formation in fatty acids were Waentig and Pescheck,[1] who classified chloroform, carbon tetrachloride, benzene, nitrobenzene, and toluene as nondissociating, and ethyl alcohol, ethyl ether, ethyl acetate, and benzaldehyde as dissociating Chlorinated solvents are particularly noted for their tendency to promote compound formation (see page 66), whereas the most strongly dissociating solvents are polar compounds such as acetone, which has long been the more or less standard solvent for fractional crystallization of fats and fatty acids in the laboratory However, at moderately low temperatures acetone is not completely miscible with liquid

[37] C E Bills *J Biol Chem* , 67, 279–285 (1926)

oils at low solvent ratios (at a solvent–oil ratio of 2 1 by weight, separation of cottonseed oil occurs at about 26°F, for example), and this somewhat restricts its usefulness in the practical separation of glycerides Methyl acetate is equivalent to acetone for the fractional crystallization of fatty acids Ethyl acetate is nearly as effective as acetone for this purpose, whereas methyl ethyl ketone and petroleum naphtha permit association to a greater degree, and are less effective at any fixed temperature, although the solubility of pure saturated acids is less in petroleum naphtha than acetone[38] However, petroleum naphtha is fully equivalent to acetone or methyl acetate if used at a crystallization temperature about 10° F lower than that at which the latter solvents are employed

Present solubility data on fatty materials are generally meager, and in some cases probably not over reliable

The solubilities reported for various fatty acids in acetone are listed in Table 21 Values in this table for the higher temperatures are selected from the publication of Ralston and Hoerr[36] Those at the lower temperatures are from Foreman and Brown[38]

The solubilities of various fatty acids in methyl and ethyl alcohol, according to Foreman and Brown and Ralston and Hoerr, are given in Table 22

Solubilities of fatty acids in petroleum naphtha (Skellysolve B) as determined by Foreman and Brown, are listed in Table 23 It should be noted that these and the previously mentioned solubility data of Foreman and Brown do not represent complete equilibrium conditions, and hence can be considered approximate only In addition to the above, Ralston and Hoerr have in the same publication reported solubility data on the common saturated acids in butanone, benzene, and glacial acetic acid

Lately, Hoerr and Ralston[38a] have reported additional data on the solubility between 0° and 60°C of the C_8 to C_{18} saturated acids in cyclohexane, tetrachloromethane, trichloromethane, ethyl acetate, butyl acetate, methanol, isopropanol, *n* butanol, nitroethane, and acetonitrile

It follows from thermodynamic considerations, and has been observed in experiments on many solid substances dissolved in liquids, that in the lower ranges of solubility there is a linear relationship between the logarithm of the solubility and the reciprocal of the absolute temperature (Within a limited range, a plot of the temperature against the logarithm of the solubility produces a substantially straight line) The above mentioned data of Ralston and Hoerr and of Foreman and Brown show that in the case of the higher saturated fatty acids dissolved in organic solvents this straight line relationship holds generally at temperatures below about 0°C Experiments of the author and co workers reveal that it also holds over

[38] H D Foreman and J B Brown, *Oil & Soap*, **21**, 183–187 (1944)
[38a] C W Hoerr and A W Ralston *J Org Chem*, **9**, 329–337 (1944)

Table 21
Solubility of Fatty Acids in Acetone

Fatty acid	Grams acid per 100 grams solvent at temperature in degrees C												
	Foreman and Brown[a]									Ralston and Hoerr			
	−70°	−60°	−50°	−40°	−30°	−20°	−10°	0°	10°	0°	10°	20°	30°
Caprylic	—	—	—	—	—	—	—	—	—	221	975	—	—
Capric	—	—	—	—	—	—	—	—	—	45 3	112	407	4660
Lauric	—	—	0 025	—	1 23	1 74	—	—	—	8 95	21 9	60 5	218
Myristic	—	—	—	—	0 174	0 433	1 07	2 27	—	2 75	6 50	15 9	42 5
Palmitic	—	—	—	—	0 048	0 134	0 280	0 715	1 77	0 60	1 94	5 38	15 6
Stearic	—	—	—	—	—	—	0 038	0 219	0 469	0 21	0 80	1 54	4 93
Arachidic	—	—	—	—	—	—	—	0 075	0 183	—	—	—	—
Behenic	—	—	—	—	—	—	—	0 010	0 051	—	—	—	—
Oleic	0 040	0 061	0 189	0 516	1 42	—	—	—	—	—	—	—	—
Linoleic	0 519	1 42	4 82	—	—	—	—	—	—	—	—	—	—
Linolenic	—	4 32 at −62°	—	—	—	—	—	—	—	—	—	—	—
Erucic	—	—	—	—	—	0 352	—	—	—	—	—	—	—
Eicosenoic	—	—	—	0 147	0 458	1 61	—	—	—	—	—	—	—

[a] Solubilities reported by Foreman and Brown are approximate only and are expressed in terms of grams acid per 100 grams solution See text page 71

Table 22

Solubility of the Fatty Acids in Alcohols

Ethyl alcohol (according to Ralston and Hoerr)

Per cent by wt	Acid	Grams acid per 100 grams solvent at temperature in degrees C						
		0°	10°	20°	30°	40°	50°	60°
99 4	Lauric	20 4	41 6	105	292	1540	∞	∞
	Myristic	7 07	9 77	23 9	84 7	263	1560	∞
	Palmitic	1 89	3 20	7 21	23 9	94 2	320	2600
	Stearic	0 42	1 09	2 25	5 42	22 7	105	400
95 0	Caprylic	262	1035	∞	∞	∞	∞	∞
	Capric	60 6	93 5	440	8980	∞	∞	∞
	Lauric	15 2	34 0	91 2	260	1410	∞	∞
	Myristic	3 86	7 64	18 9	68 7	238	1485	∞
	Palmitic	0 85	2 10	4 93	16 7	73 4	287	2280
	Stearic	0 24	0 65	1 13	3 42	17 1	83 9	365
91 1	Palmitic	0 76	1 94	4 60	15 3	—	—	—
	Stearic	0 13	0 35	0 66	2 30	13 5	68 7	—
80 8	Stearic	*ca* 0 06	0 10	0 20	0 81	3 20	50 8	238

Methyl alcohol (approximate solubilities according to Foreman and Brown)

Fatty acid	Grams acid per 100 grams solution at temperature in degrees C								
	−70°	−60°	−50°	−40°	−30°	−20°	−10°	0°	10°
Lauric	—	—	—	—	0 823	1 70	2 83	—	—
Myristic	—	—	—	—	0 153	0 344	0 826	1 84	—
Palmitic	—	—	—	—	0 020	0 063	0 146	0 396	1 31
Stearic	—	—	—	—	—	0 010	0 032	0 092	0 259
Arachidic	—	—	—	—	—	—	—	0 065	0 096
Behenic	—	—	—	—	—	—	—	0 010	0 042
Oleic	0 032	0 051	0 089	0 329	0 708	—	—	—	—
Linoleic	0 394	0 925	2 52	—	—	—	—	—	—
Linolenic	—	1 76 at −62°	—	—	—	—	—	—	—
Erucic	—	—	—	—	0 087	0 176	—	—	—
Eicosenoic	—	—	—	0 129	0 348	1 06	—	—	—

Table 23

Approximate Solubility of Fatty Acids in Petroleum Naphtha (Skellysolve B) according to Foreman and Brown

Fatty acid	Grams acid per 100 grams solution at temperature in degrees C								
	−70°	−60°	−50°	−40°	−30°	−20°	−10°	0°	10°
Lauric	—	—	—	—	—	0 379	1 07	1 51	—
Myristic	—	—	—	—	0 020	0 131	0 325	0 943	—
Palmitic	—	—	—	—	0 009	0 012	0 026	0 125	0 838
Stearic	—	—	—	—	—	—	0 010	0 024	0 131
Arachidic	—	—	—	—	—	—	—	0 048	0 056
Behenic	—	—	—	—	—	—	—	0 010	0 029
Oleic	0 024	0 042	0 104	0 483	1 18	—	—	—	—
Linoleic	0 009	0 327	1 70	—	—	—	—	—	—
Linolenic	—	0 443 at −62°	—	—	—	—	—	—	—

moderate ranges of temperature for saturated acids in the presence of the unsaturated fatty acids always found in natural fats and oils

There are but a few scattered data on the solubility of natural fats in organic solvents at low temperatures, and virtually none on pure triglycerides Bull and Wheeler[39] reported the following results in the fractional crystallization of soybean oil from acetone, at a ratio of 20 ml of

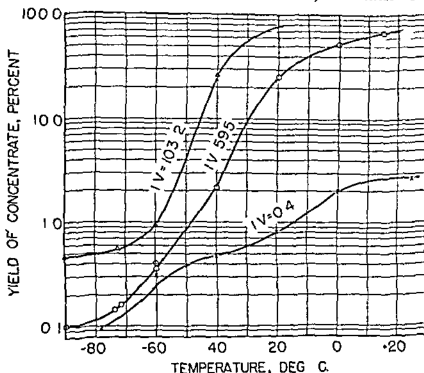


Fig 10 —Yields of soluble material from the crystallization of cottonseed oils at low temperatures from acetone, at a solvent ratio of 8 1 [40]

solvent to 1 g of oil, the yields of solids being in each case corrected for entrained solvent and oil

Temperature, °C	Per cent dissolved	Per cent undissolved
−15	98	2
−30	90	10
−40	82	18
−45	58	42
−47 5	7	93
−50	2	98
−70	2	98

Singleton and Bailey[40] have employed low-temperature fractional crystallization from solvents as a means of concentrating tocopherols from cottonseed oil, the glycerides of the oil being largely crystallized out, to leave residues high in tocopherol content The yields of tocopherol concentrates comprise a rough indication of the solubility of the oils, although the soluble matter of course consisted partially of tocopherols and other unsaponifiable material, rather than glycerides Figure 10 shows the yields obtained in crystallizing raw oil (iodine value, 103 2)

[39] W C Bull and D H Wheeler, *Oil & Soap*, 20, 137–141 (1943)

and two hydrogenated oils (iodine values 59 5 and 0 4, respectively), from acetone, a solvent–oil ratio of 8 1 by weight being employed

The following data, from the work of the same authors, indicate the relative solubilities of the oils in acetone, methyl ethyl ketone, and petroleum naphtha (Skellysolve B) Solubilities are expressed in terms of grams of soluble material per 100 g oil, all tests being carried out at −60°C, with 10 ml of solvent per g oil

Hydrogenated oil of iodine value	Acetone	Methyl ethyl ketone	Petroleum naphtha
59 5	0 40	1 15	15 6
0 4	0 31	—	0 62

It is to be noted that there are important differences in the behavior of fatty acids and triglycerides in organic solvents, which may be attributed to the difference in polarity of the acid and the glyceride molecules Since fatty acids contain the free polar COOH group they are, at low temperatures, more soluble in polar solvents such as acetone than in nonpolar solvents such as petroleum ether In the case of triglycerides, the solubilities in the two classes of solvents are reversed

The lead soaps of the saturated C_{16} and C_{18} acids are relatively insoluble in alcohol or ether, as compared with the soaps of the corresponding unsaturated acids, the common analytical methods employed in the past for the separation of these two classes of acids have made use of this difference in solubility However, the work of Brown and Stoner,[41] followed by that of Earle and Milner,[42] and others, has revealed that equally good or better separations can be performed directly upon the free acids, by the use of suitable solvents and sufficiently low crystallization temperatures

(c) *Solubility of Gases in Fats*

The solubilities of air, oxygen, nitrogen, hydrogen, and carbon dioxide in lard, corn oil, and hydrogenated cottonseed oil were determined at 23–26°C and at 43–47°C by Vibrans [43] Schaffer and Haller[44] reported measurements of the solubility of the same gases in lard, cottonseed oil, and butterfat at 40° and 60°C Parsons and co-workers[45] have determined the solubilities of nitrogen, oxygen, hydrogen, carbon monoxide, and carbon dioxide in both unhydrogenated and hydrogenated lard and cottonseed oil at temperatures ranging generally from about 30° to 150°C Since only the latter workers employed a precise experimental technique and covered an extensive range of temperature, their results alone will be quoted here in detail The values listed in Table 24 represent selected portions of their data All values in this table are in terms of Ostwald solubility

[41] J B Brown and G G Stoner, *J Am Chem Soc*, 59, 3–6 (1937) See also J B Brown, *Chem Revs*, 29, 333–354 (1941)

[42] F R Earle and R T Milner, *Oil & Soap*, 17, 106–108 (1940)

[43] F C Vibrans, *Oil & Soap*, 12, 14 15 (1935)

[44] P. S Schaffer and H S Haller, *Oil & Soap*, 20, 161–162 (1943)

[45] L B Parsons, *private communication* (1938)

coefficients, *i e* , volumes of gas dissolving at 760 mm pressure in a unit volume of oil, the volumes of both gas and oil being measured at the temperature in question

It was found that the solubility coefficients, *S*, were substantially the same for all the fats investigated and could be expressed in terms of the temperature in degrees C , *t*, by the following linear equations

$$S_{H_2} = 0\ 0295 + 0\ 000497\ t$$
$$S_{N_2} = 0\ 0590 + 0\ 000400\ t$$
$$S_{O_2} = 0\ 1157 + 0\ 000443\ t$$
$$S_{CO} = 0\ 0890 + 0\ 000400\ t$$

TABLE 24

SOLUBILITY OF GASES IN FATS[a]

Fat	Temperature °C	Solubility coefficient vol gas/1 vol oil				
		N_2	H_2	CO	O_2	CO_2
Cottonseed oil (I V = 104 3)	30 5	0 0711	0 0463	—	—	—
	49 6	0 0779	0 0540	—	—	—
	78 2	0 0891	0 0673	0 1201	—	—
	101 5	0 0976	0 0783	0 1285	—	—
	147 8	0 1183	0 1024	0 1470	—	—
Lard (I V = 70 1)	41 5	0 0765	0 0521	0 1051	—	—
	73 2	0 0879	0 0658	0 1205	—	—
	111 3	0 1038	0 0850	0 1349	—	—
	147 3	0 1206	0 1035	0 1490	—	—
Hydrogenated lard (I V < 1)	64 3	—	0 0614	—	—	0 920
	67 0	0 0844	—	0 1154	0 1450	—
	84 7	—	—	—	0 1535	—
	88 0	—	—	—	—	0 791
	139 4	0 1168	0 0979	0 1460	—	0 619

[a] According to L B Parsons, *private communication* (1938)

The data of Vibrans are in quite close agreement with those of Parsons, but the values reported by Schaffer and Haller are somewhat out of line with those of the other workers The latter noted an increase in the solubility of hydrogen in butterfat at 60° as compared with 40°C , but reported a decrease in solubility with increased temperature in the case of the other gases However, the results of Parsons clearly indicate that all of the gases except carbon dioxide are increasingly soluble in the fat as the temperature is raised Following are Parson's data, which are typical, on the absolute solubility of nitrogen in cottonseed oil

Temperature °C	Grams gas dissolved per 100 grams fat (760 mm)
30 5	0 00888
49 6	0 00929
78 2	0 00985
101 5	0 01029
147 8	0 01151

At 40°C Shaffer and Haller found all the gases to be 10% to 20% more soluble in butterfat than in lard or cottonseed oil

7. Optical Properties

(a) *Refractive Index*

The refractive indices of fats have always been a subject of much interest, because of the close relation of this characteristic to the average molecular weight and degree of unsaturation of these materials, and the ease and rapidity with which it may be determined

TABLE 25

REFRACTIVE INDICES OF FATTY ACIDS AND GLYCERIDES AT 50°C

Capric acid	1 4248	Oleic lauric lauric	1 4494
Lauric acid	1 4304	Lauric oleic lauric	1 4497
Myristic acid	1 4348		
Palmitic acid	1 4385	Oleic palmitic palmitic	1 4518
Stearic acid	1 4413	Palmitic oleic palmitic	1 4514
Oleic acid	1 4487	Oleic stearic stearic	1 4532
Elaidic acid	1 4468	Stearic oleic stearic	1 4523
Linoleic acid	1 4588		
Linolenic acid	1 4678	Caproic oleic oleic	1 4554
		Caprylic oleic oleic	1 4543
Capric capric capric	1 4408	Capric oleic oleic	1 4537
Lauric lauric lauric	1 4440	Lauric oleic oleic	1 4536
Myristic myristic myristic	1 4466	Myristic oleic oleic	1 4543
Palmitic palmitic palmitic	1 4490	Palmitic oleic oleic	1 4549
Stearic stearic stearic	1 4509	Stearic oleic oleic	1 4562
Oleic oleic-oleic	1 4586	Elaidic lauric lauric	1 4483
Linoleic linoleic linoleic	1 4683		
Linolenic linolenic linolenic	1 4779	Lauric elaidic elaidic	1 4532
Stearic lauric lauric	1 4475	[illegible]	1 4481
Lauric stearic lauric	1 4480		1 4500
			1 4518
Stearic palmitic palmitic	1 4505		1 4537
Palmitic stearic palmitic	1 4509		1 4553
Capric stearic stearic	1 4482	[illegible]	1 4510
Stearic capric stearic	1 4491		1 4522
			1 4533
Lauric stearic stearic	1 4486	[illegible]	1 4545
Stearic lauric stearic	1 4498		
Palmitic stearic stearic	1 4501		
Stearic palmitic stearic	1 4513		

Values for the refractive indices of various pure fatty acids and glycerides are recorded in Table 25 [46] To permit intercomparison, these values have all been calculated to a common temperature of 50°C , using the correction

[46] In this table values for the saturated fatty acids are taken from A Dorinson M R McCorkle and A W Ralston J *Am Chem Soc* **64**, 2739 2741 (1942) Values for the unsaturated acids are from T R Wood F L Jackson A R Baldwin and H E Longenecker, *J Am Chem Soc* **66**, 287 289 (1944) Values for the saturated simple glycerides are from R B Joglekar and H E Watson *J Indian Inst Sci* , **A13**, 119 127 (1930) Values for triolein and trilinolein are from D H Wheeler, R W Riemenschneider, and C E Sando *J Biol Chem* , **132**, 687-699 (1940) Values for the mixed glycerides and trilinolenin are taken from the publications of C G King, B F Daubert, *et al* (See footnotes 18 and 19, page 59)

factor of 0 00038 per degree C, in converting from other temperatures Numerous workers have shown that this is approximately the average decrease in the refractive index occasioned by increasing the temperature of fats or fatty acids by 1°C

The data in the table illustrate the following generalizations regarding the relationship between the refractive index and the structure and composition of fatty acids and glycerides

(a) The refractive indices of both fats and fatty acids increase with increase in the length of the hydrocarbon chains and the number of double bonds in the chains

(b) The refractive indices of simple glycerides are considerably higher than those of the corresponding fatty acids

(c) The refractive indices of mixed glycerides are in general close to those of corresponding mixtures of simple glycerides

(d) The refractive indices of monoglycerides are considerably higher than the refractive indices of the corresponding simple triglycerides

However, there are a few well marked deviations from these rules In completely saturated glycerides containing two fatty acids, the symmetrical glycerides are slightly higher in refractive index than their unsymmetrical isomers Unsymmetrical dioleins containing saturated acids of low molecular weight are abnormally high in refractive index

The presence of conjugated double bonds in the fatty acids causes a marked exaltation of the refractive index The presence of hydroxyl groups, as in ricinoleic acid, has the same effect, but to a less pronounced degree

In view of the known influence of glyceride configuration on the refractive index, it is not to be expected that the refractive indices of natural fats can be generally expressed in terms of their average molecular weight and degree of unsaturation However, a number of equations have been proposed which are of limited application and fair accuracy One of the best known of these is that of Pickering and Cowlishaw,[47] which is applicable to cottonseed oil, peanut, soybean oil, linseed oil, etc, and has the form

$$n_D^{40} = 1\,4515 + 0\,0001171\ \mathrm{I\ V}$$

Majors and Milner[48] have found that the refractive indices of soybean oils of any one crop year can be very closely correlated with the iodine value, but that there are considerable variations from one crop year to another

For data on the refractive indices of hydrogenated oils, see pages 611, *et seq*

[47] G F Pickering and G E Cowlishaw, *J Soc Chem Ind*, **41**, 74–77 (1922)

[48] K R Majors and R T Milner, *Oil & Soap*, **16**, 228–231 (1939)

(b) *Optical Rotation*

Optical activity is exhibited only by cyclic acids and their glycerides, such as those found in chaulmoogra oil, etc, and to a lesser extent by hydroxy acids, as for example ricinoleic acid It is consequently a property of little interest in oil and fat technology

(c) *Spectroscopy of Fats and Oils*

Pure fats and fatty acids are colorless and devoid of spectral properties in the visible range However, all natural fats and oils contain pigments which have characteristic absorption patterns The color of fats and oils is a matter of considerable practical importance, and figures prominently in the trading rules for these materials In the past, oils have almost invariably been graded for color by visual comparison with such standards as the Lovibond red and yellow glasses However, this method of determining color is often unsatisfactory, being particularly inadequate in the case of oils which contain considerable amounts of green or brown pigments The spectrophotometric method of evaluating color is widely used in controlling commercial refining and bleaching operations, and may be expected to eventually gain acceptance as a basis for trading rules

Unsaturated fatty acids, esters and glycerides exhibit absorptions in the ultraviolet regions Conjugated double bonds give rise to particularly marked absorption maxima, which permit the quantitative determination of conjugated acids in mixed materials by spectral means Recently, alkali isomerization (page 694) has been applied in conjunction with ultraviolet spectroscopy for the estimation of linolenic and linoleic acids in nonconjugated oils [49]

As has been mentioned previously, x-ray spectroscopy is of fundamental importance in the study of polymorphism in fatty materials, and in establishing the chain lengths of fatty acids

[49] J H Mitchell, H R Kraybill and F P Zscheile, *Ind Eng Chem , Anal Ed* , 15, 1–3 (1943)

CHAPTER IV

ROLE OF FATS IN THE DIET OF MAN

1. Fats in Human Nutrition

Despite the present large consumption of fats and oils in soap, paint, and other nonedible industrial products, the greater part of the world's fat production continues to be consumed as a human food

The per capita consumption of fats in foods in the United States was estimated[1] *to be 94 7 pounds in 1939* This amount was distributed among the various classes of food products as follows (in pounds)

Prepared fats, including butter	46 3
Meats and eggs	19 6
Dairy products other than butter	18 5
Nuts and cacao products	5 0
Grains and related products	2 7
Miscellaneous products	2 6
Total	94 7

The *fat consumed was estimated to supply approximately 33% of the* total per capita caloric intake

Fats are primarily a source of energy in the diet. They are the most concentrated of all food materials, furnishing about 9 large calories of energy per gram, as compared with about 4 calories each furnished by proteins and carbohydrates Although carbohydrates serve the same primary purpose in the diet as do fats, namely that of contributing readily *available energy, they nevertheless cannot be substituted for fats to an* unlimited degree In the case of large populations shut off from normal fat supplies by the exigencies of war, it has repeatedly been observed that the ensuing restriction of the fat intake leads to a definite, mass fat hunger This is partially explainable on the basis of the increased palatability conferred on foods by the addition of fats, and is doubtless also related to the manner in which fat delays the digestion of food, and thus prevents premature sensations of hunger after eating However, it appears that there are probably other and more deep-seated reasons for the natural craving of the human organism for fatty foods

Fats and their component fatty acids appear to perform a number of vital functions in the body which are quite unrelated to their action as

[1] U S Tariff Commission, *United States Consumption of Food in Terms of Fats, Proteins, Carbohydrates, and Calories, 1939 1943* Washington, 1944

energy-bearing materials [1a] Fatty acids in the form of phospholipides are essential constituents of many kinds of body cells Phospholipides of animal origin are distinguished by a considerable content of very highly unsaturated acids The source of these acids is unknown, however, it appears possible that they are not synthesized in the body, but must be ingested as such, in the food It has been definitely shown by Burr and coworkers[2] that linoleic or arachidonic acids are essential elements of the diet of rats, a deficiency in both of these acids leading to a form of dermatitis The necessity for these or other unsaturated acids in the diet has not been demonstrated in the case of human subjects, although the administration of highly unsaturated oils has been found beneficial in cases of eczema, and the blood of eczematous subjects has been observed to be abnormally low in unsaturated acids [3]

Fats have been reported to perform an accessory role in the absorption of calcium,[4] carotene,[5] thiamine,[6] and lactose [7] It is significant that, of the various groups of vitamins, four—A, D, E, and K—are soluble in fat rather than in water

At various times in the past, and particularly during the early days of the hydrogenation process, there has been considerable argument and discussion, largely amongst nonscientific writers, concerning the relative digestibilities of different fats It has been demonstrated, through the work of Langworthy, Holmes, Deuel, and others,[8] that there are no significant differences in the digestibility of different fats and oils except in the case of those which have melting points considerably above body temperature (*ca* 50°C and above), and are digested somewhat less completely than lower melting products It is to be noted that commercial hydrogenated fat products have melting points which are in general much lower than those of certain animal fats (*e g*, mutton fat and deer fat) which have long been accepted as wholesome products for human consumption

[1a] In this connection, see particularly H M Evans and S Lepkovsky, *J Biol Chem*, **96**, 143–156 (1932) and **99**, 231–234 (1932), and H M Evans, S Lepkovsky, and E A Murphy *ibid*, **106**, 431–449 (1934)

[2] G O Burr and M M Burr, *J Biol Chem*, **82**, 345–367 (1929), **86**, 587–621 (1930), **97**, 1–9 (1932)

[3] W R Brown and A E Hansen, *Proc Soc Exptl Biol Med*, **36**, 113–117 (1937)

[4] See for example, E J McDougall, *Biochem J*, **32**, 194–201 (1938)

[5] See, for example H E C Wilson S M Das Gupta, and Bashir Ahmad, *Indian J Med Res*, **24**, 807–811 (1937), and A R Kemmerer and G S Fraps, *J Nutrition* **16**, 309–315 (1938)

[6] W D Salmon and J G Goodman, *J Nutrition*, **13**, 477–500 (1937)

[7] [illegible]

[8]

(192

Langworthy, *Ind Eng Chem* **15**, 276–278 (1923)

It has been shown[9] that iso-oleic acids formed in fats by hydrogenation are nutritionally equivalent to ordinary oleic acid, and that mono- and diglycerides produce good growth in rats at reasonable levels of ingestion[10]

The relative nutritive values of butterfat and other edible fats have constituted the subject of much recent controversy Recent investigations in this field have been principally concerned with the rate of growth of weanling rats on different fat diets Superior growth on a butterfat diet has been reported by Harris and Mosher[11] and Boer[12] On the other hand, Euler, Euler, and Saburg[13] reported butterfat to be inferior to margarine Deuel, Movitt, Hallman, and Mattson,[14] in an extensive series of tests, could find no significant differences in a group of fats composed of butterfat, margarine, corn oil, cottonseed oil, olive oil, peanut oil, and soybean oil In a series of investigations Schantz and Boutwell *et al*[15] noted a specific growth-promoting property in butterfat and ascribed it to the saturated acid fraction, but subsequently reported that the superiority of butterfat was evident only when the carbohydrates in the diet consisted of lactose

2. Non-nutritional Functions of Edible Fats

Edible fats have certain important non-nutritional functions These functions derive principally from the distinctive physical properties of fats and oils

Large quantities of fats are used in the production of baked goods, including bread, cakes, crackers, biscuits, cookies, and pastries In this class of edible products the fat not only contributes to the food value, but also provides a highly essential lubricating action Its dispersion throughout the body of the dough prevents the gluten in the flour from forming a continuous and refractory structure, and enables the product to assume its characteristic form and texture during the baking operation In addition, a plastic fat is capable of entrapping and holding considerable air in the mixing process This air, expanding under the influence of the heat of the oven, contributes a leavening action, which is highly important in the manufacture of cakes and similar baked goods

[9] A D Barbour, *J Biol Chem*, 101, 63–72 (1933)

[10] W A Braun and C L Shrewsbury, *Oil & Soap*, 18, 249–250 (1941)

[11] [illegible] 5, 177–184 (1940)

[12] [illegible] *ol Microbiol*, 11, 180–182 (1941)

[13] [illegible] *Arkiv Kemi Mineral Geol*, B15, No 8 (1941)

[14] H J Deuel, E Movitt L F Hallman, and F Mattson *J Nutrition*, 27, 107–121 (1944)

[illegible] and E B Hart, *J Dairy Sci*, 23, 181–189 (1940) [illegible] Elvehjem and E B Hart *ibid* 23, 1205–1210 [illegible] -r, C A Elvehjem and E B Hart *ibid*, 24, 1027–1034 (1941) and 26, 429–437 (1943)

In the frying of foods, the role of the fat is essentially that of an efficient heat transfer medium, which is especially adapted to transmitting heat rapidly and uniformly to the surface of the food being cooked Frying has the advantage over other methods of cooking of being very rapid, and of neither drying the food excessively nor leaching its water-soluble constituents

The contribution of fats to the flavor and palatability of foods is very important All natural fats and oils have distinctive flavors, and the flavor of a prepared dish is often strongly influenced by the fat employed in its composition However, the effectiveness of a fat in promoting food flavor depends to a large degree simply upon the physical properties of the fat, rather than upon any flavor of its own that the fat may carry Perfectly neutral and tasteless oils, as for example, highly deodorized cottonseed oil, are used in large quantities for "seasoning" cooked vegetables, salads, sauces, gravies, etc

B. RAW MATERIALS FOR OIL AND FAT PRODUCTS

B. RAW MATERIALS FOR OIL AND FAT PRODUCTS

CHAPTER V

SOURCES, UTILIZATION, AND CLASSIFICATION OF OILS AND FATS

1. Introduction

Since oils are essential constituents of all forms of plant and animal life, they are very widely distributed in nature Every species of plant or animal develops some quantity of oil or fat during its life cycle However, the plants and animals which produce oil in sufficient quantity and in a sufficiently available form for it to form an article of commerce are relatively few in number

The largest source of oil at the present time consists of the seeds of annual plants, such as flax, soybean, cottonseed, peanut, etc Some of these plants, such as the castor plant and the oil-bearing varieties of flax, are cultivated for their oil alone Others, for example, soybeans and peanuts, produce seed which are not only a source of oil, but are also widely utilized as foods In the case of other oil-bearing plants, such as cotton and corn, the oil is merely a byproduct of a crop which is primarily grown for other purposes

The annual oil crops are, in general, products of relatively temperate climates, and require more or less careful cultivation They constitute a flexible portion of the world's oil and fat supplies, inasmuch as the production of any individual crop may be varied within wide limits from season to season

A second large source of vegetable oils comprises certain oil-bearing trees, of which the coconut, oil palm, olive, and tung are the most important The oil from the olive tree, and a portion of the oil from the palm tree, are derived from the pulp rather than the seed of the fruit All the oil-bearing trees require a relatively warm climate, and two of the most important, the coconut and oil palms, are tropical trees Both coconut and oil palms produce larger yields of oil per unit land area than do any of the annual oil crops They also flourish in the wild state, and a large proportion of the oil produced is from stands of uncultivated or semicultivated trees

The commercial land animal fats come almost entirely from three kinds of domestic animals—hogs, cattle, and sheep There are other animals, such as fowl, which are raised in large numbers, but the carcasses of these are so small that they are usually consumed without the fatty portions being separated and processed to yield a pure fat Wild land animals are

no longer a considerable source of fats except in a very few rest gions All three of the above mentioned animals thrive best and in the greatest numbers in temperate climates

The production of animal body fats is not as large as that of fats There are regions where the production of fat from the m goat, buffalo, reindeer, etc , is of local importance, but much th part of the world's milk fat production consists of butterfat, deri cow's milk The successful husbandry of dairy cows requires n temperate climate, but also an intensive agriculture, with a plentif of feedstuffs Consequently, it is largely restricted to the mo settled regions of the world, which have a high production of othe tural products

A considerable volume of oils is contributed by the sea Fish principally derived from the more numerous, small, oily fish, suc dines, herring and menhaden Most of the fish processed for oil a in the north Atlantic and north Pacific oceans Fish oils, unlik fats, are not usually by products of the preparation of carcasses f The whole fish are processed to yield oil as the primary product, residue remaining after extraction of the oil is used for animal fee fertilizer The production of fish oil is surpassed by that of w which under normal conditions ranks in volume with the major v oils Whales are taken primarily for their oil, although in recent y recovery of by products has assumed some importance Most of t oil is produced by ships operating in the Antarctic regions

2 Trends in Oil and Fat Consumption

(a) *Edible Fat Products*

The per capita consumption of fats and oils in the form of p edible products, such as butter, margarine, lard, shortenings, and sa cooking oils has steadily increased in the past 75 years in the Unite and probably elsewhere in the civilized world Consumption of t most important edible fat products in the United States, at 10 yea vals since 1870 is indicated in Table 26 Reliable data for the earli are unavailable, but it is evident that the combined consumption of margarine, shortening and lard has increased throughout the peri

It is extremely difficult to evaluate the trend in the consumption c fats in all forms A good deal of fat is consumed in milk, cream, fa nuts, vegetables, etc However, in view of the preceding data an or less similar data relative to certain European countries, it appea able that there has also been a slight increase in the over all pe consumption of edible fats It is true that less fat meat is consum than formerly, but this is probably more than compensated by a increased use of fats in such products as cooking and salad oils, sala

ings and confections In 1939, the consumption of fats in such products in the United States amounted to 426,000,000 pounds, or 3 2 pounds per capita In addition, there is now an annual consumption in this country of approximately 750,000,000 pounds of cocoa beans, which contain 50% to 55% of fat This accounts for an additional consumption of about 3 pounds of fat per capita

The continuing demand for edible fats is notable in view of a decline in the per capita consumption of other staples such as flour, meat, and potatoes, in favor of an increased consumption of fresh and canned fruits and vegetables

TABLE 26

PER CAPITA CONSUMPTION IN POUNDS OF EDIBLE FATS IN THE UNITED STATES DOMESTIC DISAPPEARANCE OF BUTTER MARGARINE, LARD, AND SHORTENINGS (COMPOUNDS AND VEGETABLE COOKING FATS) IN SPECIFIED YEARS[a]

Item	1870	1880	1890	1899	1909	1919	1929	1939
Butter	10 7	15 5	18 2	19 6	17 8	15 3	17 4	17 4
Margarine	0 0[b]	0 2[b]	0 5[b]	1 1[b]	1 2	3 4	2 9	2 3
Lard	—	—	12 0[b]	12 7	12 4	11 2	13 2	12 8
Shortenings	0 0[b]	0 1[b]	3 0[b]	4 5[b]	7 5[b]	11 7	9 9	10 7
Total	—	—	33 7	37 9	38 9	41 6	43 4	43 2

[a] Data compiled as follows *Butter*, for 1870 to 1929, from *U S Dept Agr Tech Bull* No 722, Production and Consumption of Manufactured Dairy Products, April 1940 ', for 1939 from *Fats and Oils Situation* U S Dept Agr, B A E, Feb, 1943 *Margarine*, for 1909 to 1939, computed from data on quantity withdrawn for general use plus withdrawals for use in federal institutions, as reported annually by the Commissioner of Internal Revenue *Lard* for 1899 to 1939, from "Livestock, Meats and Wool Market Statistics and Related Data, 1942," U S Dept of Agr, F D A *Shortenings* for 1919 to 1939 from *Fats and Oils Situation* (June 1943) Figures for other years are very rough estimates only, and are derived from data supplied by G M Weber and C L Alsberg *The American Vegetable Shortening Industry*, Food Research Institute Stanford University, 1934, and K Snodgrass, *Margarine as a Butter Substitute*, Food Research Institute, 1930

[b] Rough estimate only

In the manufacture of edible products there has been a pronounced trend from animal to vegetable oils, which will probably continue for some time Both shortening and margarine are now largely made from vegetable oils In 1940, 93% of the oils used in the United States in the manufacture of edible fat products other than lard and butter were of vegetable origin In Europe there has been also a tendency to replace land animal fats with whale oil, which was produced in huge quantities from about 1929 onward, and widely utilized in margarine manufacture

(b) *Nonedible Fat Products*

In the general absence of adequate statistics over a long period of time, it is difficult to determine the trends of consumption in nonedible fields

Plainly, however, the per capita consumption of oils in soaps and other detergent products has been steadily mounting for a long time, and will doubtless continue to do so for a long time to come Increase in soap consumption always follows the spread of civilization through the world, and there is no indication that fats will be soon replaced as raw materials for the manufacture of detergents

The situation is somewhat different with respect to the use of oils in paints and other protective coatings There is a tendency to replace wooden structures with buildings of brick, stone, and compositions which require no paint The use of stainless and rustless metals and plastics for miscellaneous structural purposes is also increasing, and these generally require no protective coating Furthermore, there has been a significant development in recent years of synthetic coating materials, from nonfatty sources It seems possible, therefore, that the use of oils in protective coatings may have reached its peak and will henceforth somewhat decline

Fatty oils are now seldom used alone as lubricants for machinery, having been replaced by mineral oil products However, in many classes of lubricants, including particularly the heavier greases, fatty materials are still an important ingredient The demand for all lubricants has increased tremendously within the past several decades Therefore, even though they have declined in relative importance in comparison with petroleum products, it is doubtful whether the absolute consumption of fats in lubricants has diminished appreciably, if at all

The use of fats as illuminants has diminished very greatly As burning oils they have been largely replaced by petroleum, in countries in which petroleum is available, although they are still used to some extent in the manufacture of candles

Altogether, it appears that the nonedible use of fats is probably expanding somewhat and will probably continue to expand Fats are at present the cheapest and most satisfactory source of long hydrocarbon chains which are definite in structure and reactive in nature Such structural units are essential in the manufacture of a great variety of useful substances While it is true that long hydrocarbon chains are also found in petroleum, and that methods may be eventually developed for modifying these chains to make them properly reactive, the fact remains that the preparation of fully satisfactory fat substitutes from petroleum remains far from accomplishment Furthermore, the world's reserves of cheap petroleum are not inexhaustible, and once exhausted cannot be replaced, whereas oils and fats may continue to be grown indefinitely.

3. Classification of Fats and Oils

It is customary to classify the various fats and oils on the basis of their iodine values, into nondrying, semidrying, and drying oils However, this

system of classification fails to take into account a number of important distinctions within the three broad classes. From the standpoint of their industrial utilization they are more rationally divided into the following groups

(a) The Milk Fat Group

The fats of this group are derived entirely from the milk of domesticated land animals. All of the various members of the group are very similar in composition. The principal acids in the milk fats are not different from those in many other fats, consisting of oleic, palmitic, and stearic acids. These fats are distinguished from others, however, by subordinate contents of a very wide assortment of low molecular weight acids, which range downward in number of carbon atoms to butyric acid. They are the only fats which contain butyric acid in appreciable quantities. In addition to the lower molecular weight saturated acids, the milk fats also contain small amounts of monoethenoid acids with 10, 12, 14, and 16 carbon atoms, as well as traces of highly unsaturated acids of the arachidonic type. These fats are utilized wholly for edible purposes, being barred from other uses by their expensiveness in comparison with other fats.

(b) The Lauric Acid Group

The fats of this group are all derived from the seeds of species of palms, such as the coconut, oil palm, babassu, etc. They are distinguished from other fats by their high content of lauric acid (40–50%). They contain smaller amounts of saturated acids with 8, 10, 14, 16, and 18 carbon atoms. Their unsaturated acids are minor in amount and consist of oleic and linoleic acids; they are the least unsaturated of all the fats. Because of the low molecular weight of their acids, these fats possess the distinctive combination of a very low degree of unsaturation and a relatively low melting point. For this reason they are valuable edible fats for certain purposes. Their sodium soaps are hard and stable toward oxidation, but also freely soluble, hence they are particularly prized for soapmaking. They are also the sole source of low molecular weight fatty acids for the preparation of certain important fatty acid derivatives. Because of their tropical origin, and the fact that the plants are perennial in growth and do not require intensive cultivation, they are relatively plentiful and cheap.

(c) The Vegetable Butter Group

The vegetable butters are obtained from the seeds of various tropical trees. They are somewhat similar to the lauric acid oils in their property of softening and melting over a narrow temperature range. Their distinctive consistency is not due to the presence of low molecular weight acids, however, but rather to the particular configuration of their glycerides. Although they all contain 50% or more of saturated C_{14} to C_{18} acids, these

acids are grouped with the unsaturated acids (oleic and linoleic) in the glycerides in such a manner as to almost wholly avoid the presence of trisaturated glycerides The representative fat of this group is cocoa butter The vegetable butters are relatively high-priced fats and are used chiefly in the manufacture of confections and pharmaceutical products

(d) *The Animal Fat Group*

This group consists of the body fats of domestic land animals (lard, tallow, etc) These fats are characterized by a high content of C_{16} and C_{18} fatty acids and a comparatively low degree of unsaturation Their unsaturated acids consist almost entirely of oleic and linoleic acids Although similar to the vegetable butters in fatty acid composition, they are quite different with respect to the configuration of their glycerides They contain considerable proportions of fully saturated glycerides, which give them an extended plastic range They are important edible fats, such portions of the production as are suitable are generally used for this purpose However, because they are in some cases derived from animals or parts of carcasses which are unfit for consumption as food, a considerable part of the total production appears on the market as inedible fats These are principally used in the manufacture of soap, of which they may be considered the basic ingredient

The animal fats are generally priced somewhat below most of the vegetable oils

(e) *The Oleic-Linoleic Acid Group*

This is the largest of the various groups and the one within which there is the most variation in the composition and characteristics of the individual oils The oils of this group are all of vegetable origin They consist predominantly of unsaturated fatty acids, in most cases the saturated acids comprise less than 20% of the total Their unsaturated acids consist of oleic and linoleic acids Linolenic acid or other acids more unsaturated than linoleic are wholly absent

As is the case with other vegetable oils, the fatty acids of the oleic-linoleic acid oils are so distributed as to form negligible proportions of trisaturated glycerides Consequently, most members of the group are liquid except at quite low temperatures Most of the oils, for example, cottonseed and peanut oils, are derived from the seeds of annual plants Olive and palm oils, however, are obtained from tree fruits, and kapok oil is expressed from the seed of a tree Most of the plants producing oils of this group grow best in a relatively warm climate

The oleic linoleic acid oils are the most widely useful and the most adaptable of all the fats and oils They are not sufficiently unsaturated to have more than weakly drying properties, so they are not used to any extent in

paints or other protective coatings However, they are excellent edible oils Since they contain no linolenic or other highly unsaturated acids, they are free of any serious tendency toward flavor reversion Although normally liquid, they may be converted by hydrogenation to plastic fats of any desired degree of hardness Thus the same oil may serve equally well for the manufacture of either liquid or plastic edible fats Palm oil produces firm, stable soaps of desirable properties Most of the other oils of the group are too much sought after as edible fats to find much use in soapmaking, and in addition are too unsaturated to yield soaps of a desirable degree of hardness and stability They may be hydrogenated, however, to form suitable hard soap fats, and a certain amount of these oils is regularly used in the preparation of soft soaps and in blends with harder fats

The oleic-linoleic acid oils may in general be considered medium priced fats, somewhat more expensive than most other vegetable oils or the less choice animal fats, but much less expensive than butterfat

The more important members of the oleic-linoleic acid group include cottonseed, peanut, sesame, corn, sunflower, olive, and palm oils

(f) *The Erucic Acid Group*

The members of this group, of which only mustard, ravison, and rapeseed oil are commercially important, are distinguished by a high content of erucic acid They also contain a small amount of linolenic acid These oils are produced principally in certain Far Eastern countries, where they are used for edible and other purposes In the Occident they are principally utilized in nonedible fields Their principal use in the United States is in the manufacture of lubricants

In comparison with most other vegetable oils, these oils are normally cheap

(g) *The Linolenic Acid Group*

The oils of this group are distinguished by containing some amount of linolenic acid, in addition to oleic and linoleic acids The most important members of the group are derived from the seeds of annual plants Unlike most of the oil-bearing plants discussed previously, the plants which produce these oils thrive best in a relatively cool climate

The linolenic acid oils all have drying properties, hence are used in paints and similar products Due to their tendency to revert in flavor with slight oxidation, these oils are not considered as desirable for edible purposes as the oleic-linoleic acid oils, although in the case of soybean oil most of the oil produced is used in food products They are used relatively little for soapmaking, for reasons similar to those which limit the use of the oleic-linoleic acid oils for the same purpose They are usually somewhat cheaper than most of the oleic-linoleic acid oils

The most important members of the group are linseed, perilla, soybean, and hempseed oils

(h) *The Conjugated Acid Group*

The oils of this group are differentiated from others by containing fatty acids with conjugated double bonds The commercially important members of the group are tung oil, which consists largely of elaeostearic acid, and oiticica oil, which consists largely of licanic acid Both of these oils are derived from the seeds of trees requiring a mild climate

Because of the conjugate position of the double bonds in their fatty acids, which favors oxidation and polymerization, these oils dry more strongly and rapidly than ordinary drying oils Consequently, they are in much demand for the manufacture of certain varieties of varnishes, enamels and other protective coatings They are unsuitable for either edible purposes or soapmaking Since China is the single large source of an oil of this type, the price of the conjugated acid oils is largely dependent upon the availability of the Chinese crop of tung oil At the present time, with Chinese tung oil eliminated from world markets by war conditions, the price of these oils is much above that of any vegetable oil save olive oil

(i) *The Marine Oil Group*

These oils are distinguished by the diversity of their unsaturated fatty acids They contain large proportions of C_{16}, C_{20}, and C_{22} unsaturated acids in addition to the C_{18} acids which are common in other fats, and some of their C_{20} and C_{22} acids contain more than three double bonds The group comprises both fish oils and marine mammal oils, such as whale oil

As a class, the marine oils are among the cheapest of all fats and oils They are used in edible fat products, in soap, and in protective coatings, although in none of these fields are they considered as desirable raw materials as ordinary vegetable and animal fats

Fish liver oils constitute a special class of oils which are highly valuable as a source of vitamins A and D, and are but little used for ordinary edible or industrial purposes

(j) *The Hydroxy Acid Group*

The sole representative of this group is castor oil, which is unique in consisting largely of glycerides of ricinoleic or hydroxyoleic acid Due to its high content of this unusual acid, castor oil is different in many respects from any other oil It is not edible and not used to any extent in soapmaking By the dehydration process it can be converted to a conjugated acid oil somewhat similar to tung or oiticica oil, hence it is extensively used in the protective coating industry It also has many specialty uses, as a lubricant, as an oil for sulfonation, as a fluid for hydraulic systems, etc

CHAPTER VI

PRODUCTION AND CONSUMPTION OF PRIMARY FATS AND OILS

1. Milk Fats

(a) *Butterfat and Butter from Cows' Milk*

The butterfat content of cows' milk is somewhat variable but is ordinarily between about 3% and 5% In 1940 the average content of butterfat in milk produced in the United States was reported to be 3 95%[1] The yield of butterfat obtained from a cow depends upon the feed of the animal and also upon the extent to which breeding and selection have been carried in order to obtain animals which will give a maximum fat production The estimated yield of butterfat per cow in the United States in 1940 varied from 98 pounds in the state of Louisiana to 264 pounds in California, with an average for the nation of 183 pounds[1] Production is generally somewhat higher than this in the dairying sections of Europe The yield of butterfat per cow in New Zealand in 1936 was reported to be 234 pounds[2]

The production of butter in different countries in average years during the period 1929-1936 is shown in Table 27[2] It is to be noted that a number of countries, including Russia, are omitted from the tabulation because of the absence of information as to their production Consequently, the normal world production of butter is somewhat greater than the total of the figures shown in the table In the years immediately preceding 1939, it was estimated to have been about 4,000,000 metric tons or 8,800,000,000 pounds annually[2] International trade in butter, in terms of net imports or exports in specified countries in 1937, is shown in Table 28[2]

Of the larger butter-consuming countries of the world, the United States, Canada, and France normally produce approximately their own requirements, and neither import or export any considerable quantity Denmark and the Netherlands, Australia and New Zealand, and the Scandinavian countries all have a large exportable surplus, practically all the exported butter goes normally either to the United Kingdom, where imports amount to nine tenths of the butter consumed, or to Germany, where imports are about one sixth the total consumption Imports of butter into the United States are now subject to a duty of 14 cents per pound, hence are negligible

[1] U S Dept Agr, *Agricultural Statistics* Washington (1943 and preceding years)

[2] International Institute of Agriculture, *Oils and Fats Production and International Trade* Rome, 1939

The figures of both Tables 27 and 28, it will be noted, are in terms of butter, which contains 80–85% butterfat, rather than in terms of actual fat

TABLE 27

BUTTER PRODUCTION IN DIFFERENT COUNTRIES OF THE WORLD IN SPECIFIED YEARS DURING THE PERIOD 1934–1936

Country	Year	Production million pounds	Country	Year	Production million pounds
United States	1935	2185	Switzerland	1935	63
Germany	1935	996	Finland	1935	53
France	1935	475	Austria	1936	49
Australia	1935	470	Union of South Africa	1936	47
Denmark	1934	402	Brazil	1935	39
New Zealand	1936	377	Egypt	1935	39
Canada	1935	348	Lithuania	1936	35
Netherlands	1936	244	Esthonia	1936	30
Ireland	1935	183	Norway	1936	25
Czechoslovakia	1936	152	Hungary	1936	22
Sweden	1936	147	Spain	1933	16
Belgium	1936	143	Syria	1936	16
Poland	1936	110[a]	Greece	1936	13
United Kingdom	1936	106[a]	Chile	1936	9
Italy	1934	100	Japan	1936	6
Latvia	1935	70	Algeria	1930	5
Argentina	1936	70	Peru	1929	2

[a] Rough estimates only

TABLE 28

INTERNATIONAL BUTTER TRADE IN 1937, IN TERMS OF NET IMPORTS OR EXPORTS IN DIFFERENT COUNTRIES

Country	Net exports million pounds	Net imports million pounds	Country	Net exports million pounds	Net imports million pounds
Denmark	337	—	Cuba	<1	—
New Zealand	333	—	United Kingdom	—	1041
Australia	183	—	Germany	—	191
Netherlands	119	—	United States	—	10
Sweden	52	—	Netherlands East Indies	—	10
Latvia	42	—	Switzerland	—	6
Ireland	41	—	Belgium	—	5
Russia	32	—	Italy	4	—
Finland	31	—	Algeria	—	4
Esthonia	29	—	Egypt	—	2
Argentina	19	—	British Malaya	—	2
Poland	18	—	Philippine Islands	—	1
Austria	8	—	Trinidad	—	1
France	5	—	Spain	—	<1
Canada	4	—	Czechoslovakia	—	<1
Union of South Africa	1	—	Greece	—	<1
Norway	<1	—	China	—	<1
Yugoslavia	<1	—	Peru	—	<1

In the United States, most of the butter is produced in the Middle Western states In 1940, the production of creamery butter in factories in the principal producing states was as indicated in Table 29 The average

TABLE 29

CREAMERY BUTTER PRODUCTION IN THOUSAND POUNDS IN DIFFERENT STATES OF THE U S IN 1940[a]

Minnesota	311,153
Iowa	245 312
Wisconsin	183 103
Michigan	95 766
Nebraska	83 327
Missouri	82 204
Illinois	80 642
Ohio	80 384
Kansas	75 806
Indiana	70 650
California	69 865
North Dakota	58 416
Oklahoma	51,151

[a] U S Dept Agr , *Agricultural Statistics*, Washington

TABLE 30

PRICES RECEIVED BY FARMERS FOR BUTTERFAT IN THE U S , 1932–1942[a]

Year	Price cents/lb	Year	Price cents/lb
1932	17 9	1937	33 2
1933	18 8	1938	26 2
1934	22 7	1939	23 8
1935	28 1	1940	28 0
1936	32 2	1941	34 4

[a] U S Dept Agr , *Agricultural Statistics*, Washington

TABLE 31

AVERAGE WHOLESALE BUTTER PRICES IN CENTS PER POUND AT DIFFERENT MARKETS IN RECENT YEARS[a]

Year	New York (92 score)	London (Danish)	London (New Zealand)	Copenhagen	New Zealand (av of four markets)
1920	61 5	—	—	—	—
1924	42 6	—	—	—	—
1928	47 4	—	—	—	—
1932	21 0	18 5	15 9	15 2	15 8
1933	21 6	19 7	15 4	14 9	15 2
1934	25 7	22 1	16 4	16 4	16 9
1935	29 8	24 6	19 9	19 1	20 5
1936	33 0	26 5	22 4	20 8	22 4
1937	34 4	28 1	24 5	22 5	23 2
1938	28 0	28 4	25 6	22 8	23 8
1939	26 0	—	—	22 0	24 3
1940	29 5	—	—	27 4	21 3
1941	34 3	—	—	34 1	22 2

[a] U S Dept Agr , *Agricultural Statistics*, Washington

prices received by farmers in the United States for butterfat during the period 1932 to 1942 are shown in Table 30 Average wholesale prices for butter at different world markets in recent years are listed in Table 31.

(b) *Fat from the Milk of Other Animals*

Data do not appear to be available covering the production of fat from the milk of animals other than cows Probably the largest production of such fat is that of ghee from the milk of buffaloes, which is known to reach considerable proportions in India A certain amount of goat's butter is produced in certain regions of the world, including parts of the United States, and there is possibly a limited production and consumption of milk fat products from the milk of a few other domesticated animals

2. Lauric Acid Oils

(a) *Coconut Oil*

The most important of the lauric acid oils is coconut oil, which is a product of the coconut palm, *Cocos nucifera* This palm is extremely widely distributed throughout the tropical zone It is to be found in the greatest numbers, however, in the coastal regions of India, Ceylon, British Malaya, and the tropical Pacific islands, including the Netherlands East Indies and the Philippines

Formerly coconuts were entirely a product of trees growing in the wild or semiwild states, but now a considerable portion of the coconut oil entering into commerce comes from nuts grown on large plantations The yield of oil per acre from well cultivated coconut trees is much greater than is to be realized from any of the annual oil seed crops The trees are usually planted at a density of 55–60 trees per acre, and it is said that groves in good production will yield an average of 60 coconuts per tree yearly, or 3300 coconuts per acre The average nut will yield about 0 5 pound of dried copra, which will in turn yield about 63% of oil Consequently an acre of coconuts may be expected to yield not less than 1650 pounds of copra or 1040 pounds of coconut oil Considerably higher yields have been reported in many instances

The trees begin to bear in about 6 years after planting and reach their productive peak in 8 to 10 years The nuts are harvested throughout the year After harvesting they are split open and then dried, either in the sun or by artificial means In the process of drying the oil bearing kernel lining the inside of the shell shrinks and separates from the shell The dried kernel constitutes the copra of commerce It is desirable to reduce the moisture content of copra to less than about 8% in drying, in order to eliminate the possibility of subsequent excessive enzyme action and mold growth, with the consequent development of large amounts of free fatty acids in the oil Much copra is dried by crude and poorly controlled native methods, which accounts in part for the relatively high free fatty acid content of coconut oil as compared with the oils produced from the seeds of

annual plants The average yield of oil obtained by crushing dry copra is considered to be approximately 63%[3]

There is a good demand in the United States and Europe for the cake remaining after expression of the oil, for use as a livestock feed In the producing regions the cake is of little value, consequently coconut oil, like other tropical seed oils, is largely exported in the form of oil bearing material rather than as an oil Before 1940, approximately 40% of the copra from Ceylon, 60% of that from the Philippines, 70% of that from British Malaya, and 95% of that from the Netherlands East Indies was exported for crushing

In addition to their use as an oil-producing material, coconuts are grown and consumed as a staple article of diet by many millions of people Because of the general lack of statistics covering consumption in the growing regions, it is impossible to formulate any reliable estimates of the total coconut or coconut oil production of the world The exports of copra and oil from the producing regions, however, (Table 32) reflect quite accurately the consumption of the oil in the nonproducing regions of the world In 1938, international trade in coconut oil and copra amounted to 2,467,000,000 pounds in terms of oil

Since 1934 there has been an excise tax of 3 cents per pound on the first domestic processing of coconut oil entering the United States from the Philippines, and a similar tax of 5 cents per pound on oil derived from copra from most other sources There is also a 2-cent duty on oil from foreign possessions As a consequence, the copra and coconut oil entering the United States between 1934 and 1941 came almost entirely from the Philippines

The principal use for coconut oil in the United States is in the manufacture of soaps Formerly a large volume of oil found its way into margarine, but its use in this product has declined greatly in recent years A considerable quantity is consumed in confections and other edible products of a specialty nature Relatively little coconut oil is consumed in shortening, and the amount used in paints and similar products is negligible

(b) *Palm Kernel Oil*

Palm kernel oil is derived from the seed kernels of the so-called oil palm, *Elaeis guineensis* This palm is native to the tropical regions of the West African coast It has been transplanted to the Netherlands East Indies and British Malaya, however, and cultivated there on plantations on a very wide scale

The oil palm is distinctive among oil-bearing plants in producing two

[3] U S Tariff Commission, *Fats, Oils, and Oil Bearing Materials in the United States* Washington, 1941

TABLE 32

INTERNATIONAL TRADE IN COCONUT OIL AND PALM KERNEL OIL IN 1937-1938
(Including trade in oil bearing materials, calculated to their oil equivalent on the basis of copra = 63% oil and palm kernels = 45% oil)[a]

Country	Coconut oil (1938) million pounds		Palm kernel oil (1937) million pounds	
	Net exports	Net imports	Net exports	Net imports
Producing countries				
Philippine Islands	840	—	—	—
Netherlands Indies	803	—	41	—
Ceylon	275	—	—	—
British Malaya	207	—	—	—
New Guinea	104	—	—	—
Mozambique	54	—	—	—
Fiji	47	—	—	—
Solomon Islands	32	—	—	—
Tonga	18	—	—	—
British India	—	115	—	—
Nigeria	—	—	340	—
Belgian Congo	—	—	95	—
French W Africa	—	—	81	—
Sierra Leone	—	—	78	—
French Cameroons	—	—	37	—
Other countries	87	—	70	—
Consuming countries				
United States	—	680	—	39
Germany	—	387	—	320
United Kingdom	—	242	—	151
France	—	193	—	70
Czechoslovakia	—	92	—	19
Sweden	—	92	—	—
Denmark	—	72	—	36
Norway	—	63	—	—
Netherlands	—	55	—	34
Other countries	—	290	—	40
TOTALS	2467	2281	742	714

[a] U S Dept Agr, *Agricultural Statistics*, Washington Imperial Economic Committee, *Vegetables Oils and Oilseeds*, H M Stationery Office, London, 1938

TABLE 33

FACTORY CONSUMPTION OF COCONUT OIL IN MILLION POUNDS IN THE U S IN RECENT YEARS ACCORDING TO MAJOR CLASSES OF USES[a]

Year	Shortening	Margarine	Other edible products	Soap	Paints etc
1931	34 1	133 1	53 0	340 5	<0 5
1932	8 3	123 2	40 9	353 5	<0 5
1933	7 1	150 1	69 3	322 3	<0 5
1934	9 0	123 7	78 6	341 1	<0 5
1935	44 0	174 3	87 1	229 7	<0 5
1936	38 4	150 5	60 0	307 4	1
1937	12 5	73 8	49 9	252 2	1
1938	26 2	89 5	61 5	343 0	<0 5
1939	20 7	38 5	43 9	388 9	1
1940	17 6	21 8	54 7	396 9	1

[a] U S Tariff Commission, *Fats, Oils and Oil Bearing Materials in the United States* Washington, 1941

different varieties of oil, each in commercially important quantities, from the same plant. Palm oil is expressed from the pulp of the palm fruit, while palm kernel oil is obtained from the seeds of the fruit. The two oils are entirely different in their composition and their characteristics, only the kernel oil contains lauric and other low molecular weight fatty acids.

On the West African coast, where the producing trees grow principally in the wild state, most of the palms yield a fruit with a relatively large seed and a correspondingly thin layer of pulp. In this region, the production of palm kernels is of as much importance as that of palm oil. In the South Pacific region, where production is entirely from plantations, the varieties with a small seed and a thick coat have been selected for cultivation and the kernels are only a by-product of the palm oil industry.

Palm fruits contain 35% to 60% of seed, and 6% to 13% of kernels, depending on the variety. The plantations of Sumatra and Malaya are said to yield 450 to 700 pounds of kernels per acre, equivalent to 202 to 315 pounds of oil.[2] The average yield of oil from palm kernels is about 45%.[3]

After the palm seeds are separated from the pericarp, either before or after expression of oil from the latter, they are customarily air dried for an extended period, both in order to facilitate the shelling operation and to inhibit enzyme action and mold growth in the kernels. They may usually be air dried to a moisture content of about 8% in the producing regions. The seeds are cracked, by native hand labor or in centrifugal machines, and are then bagged for exportation.

Practically all of the crushing of palm kernels is carried out in Europe, and likewise most of the oil is consumed there. Since palm oil is always obtained in connection with the production of palm kernels, there is little incentive for the more difficult extraction of kernel oil by the natives. The exports of kernels from the producing regions accordingly represent practically the entire world production of the oil. In 1937 exports of kernels amounted to 1,650,000,000 pounds, equivalent upon the basis of a 45% oil yield, to 742,000,000 pounds of oil (see Table 32).

A duty of 0.5 cent per pound imposed on edible palm kernel oil imported into the United States, in addition to an excise tax of 3 cents per pound on the first domestic processing, has resulted in limiting imports in recent years largely to a denatured, inedible product.

(c) *American Palm Kernel Oils*

There are a number of wild growing Central and South American palms which yield kernel oils of the lauric acid type, and which have assumed increasing importance within recent years as actual or potential sources of oil.

Babassu oil is obtained from the kernels of a species of Brazilian palm, which has been variously given the names *Orbygnia speciosa*, *Attalea spe-*

ciosa, Orbygnia barbosiana, etc The principal kernel producing areas are the states of Maranhao and Piahui The babassu palm is both hardy and prolific and the trees in bearing are believed to number literally in the billions They constitute the largest potential source of oil in the world

The production of babassu kernels has been limited in the past by a lack of transportation facilities in the producing areas, and by the mechanical difficulties involved in cracking the very tough, thick shells, and separating the kernels No satisfactory machines have been developed for the purpose, and thus far, all or almost all of the babassu kernels reaching the market have been separated by hand

TABLE 34
AVERAGE PRICES IN CENTS PER POUND OF THE LAURIC ACID OILS IN THE U S IN RECENT YEARS[a]

Year	Coconut oil Manila crude tanks San Francisco	Palm kernel oil bbl New York (crude)[b]	Babassu oil tanks New York crude	Cohune oil tanks New York crude
1929	7 1	8 4	—	—
1930	5 9	—	—	—
1931	3 9	5 6	—	—
1932	3 2	4 8	—	—
1933	3 0	4 3	—	—
1934[c]	4 6	5 3	—	—
1935	7 4	7 5	—	—
1936	8 0	8 1	—	—
1937	9 0	9 0	—	—
1938	6 1	6 9	—	—
1939	6 1	6 5	—	—
1940	5 6	—	—	—
1941	8 4	—	—	—
1942[d]	11 0	11 4	11 1	11 1

[a] U S Dept Agr *Agricultural Statistics* Washington R M Walsh U S Dept Agr B A E *private communications* A Dewees *U S Dept Agr Statistical Bull* No 59 (1937)
[b] F [illegible]
[c] F [illegible] ound which [illegible]
[d] Government controlled price [illegible] f bulk, duties and taxes paid

The babassu, in common with other species of *Attalea*, does not have a fleshy pericarp like that of the oil palm The dry nuts, which average about 3 4 per pound, yield an average of about 6 kernels, which constitute from 8 9% of the weight of the whole nut The kernels contain an average of about 67% of oil, of which about 63% is obtainable by expression [3]

The production of babassu kernels in Brazil amounted to 137 000,000 pounds in 1939, equivalent to about 87,000 000 pounds of oil [4,5] Of the total production of kernels, 108,000 000 pounds, equivalent to 68,000 000

[4] Brazilian Ministry of Foreign Affairs Brazil, *An Economic Social and Geographic Survey* Rio de Janeiro 1941
[5] U S Vegetable Oil Mission to Brazil Report Washington 1942

• pounds of oil, were shipped to the United States Of the oil produced in Brazil, 12,000,000 pounds were also exported to the United States

Other American palms which at present produce kernel oil in somewhat lesser quantity than the babassu include the tucum (*Astrocaryum tucuma*), murumuru (*Astrocaryum murumuru*), ouricuri (*Syagrus coronata*), cohune (*Attalea cohune*), and coyol (*Acrocomia mexicana*) Of these, the first three are found principally in Brazil, whereas the latter two grow in Central America Certain species of *Acrocomia* are also to be found in Colombia and Venezuela Some of the American palms are large potential sources of oil but their exploitation has been hampered by the same difficulties as have been encountered in the production of babassu oil Imports of tucum and murumuru kernels into the United States in 1939 amounted to 9,810,000 pounds and 7,500,000 pounds, respectively The oil equivalent of this amount of tucum kernels is about 4,300,000 pounds, that of the murumuru kernels is about 2,700,000 pounds

TABLE 35

SOURCES OF COCOA BEANS IMPORTED INTO THE U S IN 1940[a]

Country	Mill on pounds	Country	M ll on pounds
Gold Coast	271 5	Ecuador	20 1
Brazil	180 3	Other countries of the	
Nigeria	138 2	Western Hemisphere	30 4
Dominican Republic	46 9	Other countries of the	
Venezuela	24 4	Eastern Hemisphere	17 2

[a] A F Sievers and E C Higbee *U S Dept Agr*, *Foreign Agr Rept* No 6, Washington (1942)

3 Vegetable Butters

The most important of the vegetable butters is cocoa butter, which is obtained from the seeds or "beans" of the tree, *Theobroma cacao* This tree is native to tropical America, but is now also cultivated to a large extent on the west coast of Africa, and to a lesser extent in a few other tropical areas Data relative to the world production of cocoa butter or international trade in this item are lacking In 1940, 729,000,000 pounds of cocoa beans were imported into the United States from the sources indicated in Table 35

The beans contain slightly over 50% of cocoa butter Most of the beans are consumed in the form of chocolate, but a further considerable quantity are pressed for the manufacture of cocoa butter and breakfast cocoa A certain amount of beans or pressed residue is solvent extracted, in the production of fat free residues for the manufacture of theobromine and "cola" type soft drinks Exports of cocoa butter from the United States amounted in 1940 to 18,700,000 pounds

There are a number of other fats obtained from the seeds of various tropical trees, which are quite similar to cocoa butter These include Borneo tallow (*Shorea stenoptera*), which comes from British Malaya, the East Indies and adjacent regions, Chinese vegetable tallow (*Stillingia sebifera*), which is produced in India and China, and Shea butter (*Butyrospermum parkii*), from West Africa None of these fats are produced in quantities approaching that of cocoa butter They are consumed entirely in Europe and are not found on the American markets

Besides cocoa butter the only vegetable butter produced in the Western hemisphere in any quantity is ucuhuba butter, which is obtained from the seeds of the tree *Virola surinamensis*, of tropical South America A production of about 3,000,000 pounds of this fat was reported by Brazil in 1940[6] largely from the state of Para

Cocoa butter is used as a confectionery fat and to some extent in the manufacture of certain pharmaceutical products The other vegetable butters are used as confectioners' fats and for soapmaking

The price of cocoa butter in the United States has recently been as follows April, 1940, 13 cents per pound, April, 1941, 24 cents per pound, April, 1942, 25 5 cents per pound, April, 1943, 25 cents per pound

4 Animal Fats

(a) *Lard*

Lard, the body fat of the hog, is the most important of the animal fats. The yield of fat per animal depends upon the manner of cutting up and trimming the carcass, as well as the breed and condition of the animal However, according to the usual practice in North American slaughter houses, the average yield of lard per hog is approximately 14% of the live weight of the animal In 1940, in federally inspected establishments in the United States, the average weight of lard produced per hog was 30 4 pounds[6] Much hog fat is of course consumed in the form of pork All pork is relatively high in fat content and some cuts, such as salt pork and bacon, contain much more fat than all other dry substances combined

In order for hogs to attain a heavy weight quickly, with a large proportion of fat, it is essential that they be provided with a diet high in carbohydrates As a cheap, efficient, and concentrated source of this food element, corn is unrivalled Consequently, the great lard producing regions of the world are to a considerable extent those best adapted to the growing of corn

The annual world production of lard has been estimated as approximately 2,000,000 metric tons, or 4,400,000,000 pounds[7] Statistics on lard pro-

[6] U S Dept Agr, *Agricultural Statistics* Washington (1943 and preceding years)

[7] International Institute of Agriculture, *Oils and Fats Production and International Trade* Rome 1939

duction in many parts of the world are not available, however, and this estimate can be regarded as only a rough one

With the exception of the years between 1935 and 1939, when hog production was restricted by governmental control, the lard production of the United States has for a good many years been between two and three billion pounds annually At least half of the world's lard supply, therefore, is normally produced in the United States, where hog raising is largely centered in the great corn-hog belt of the middle-western states

Germany is probably the second largest lard-producing nation The production of hog fats was reported to be about 1,000,000,000 pounds in Germany in 1936[7] About half this amount, however, consisted of salted fat pork rather than lard

A second great corn- and lard-producing district is the Danube valley Hungary, Yugoslavia, and Roumania all render large quantities of lard The Russian production of lard is known to be large, but no statistics are available concerning it In some of the European countries, including Great Britain, Denmark, and Poland, considerable numbers of hogs are raised, but comparatively little lard is produced, as the hogs are not of breeds that yield much lard, and are fed a high protein diet for the production of lean pork China, Manchukuo, and Brazil all have large hog populations, but do not appear to have a corresponding output of lard.

For many years the major portion of the lard entering international trade has come from the United States Great Britain, Germany, Cuba, Czechoslavakia, and Mexico are normally the principal importing countries During the period of restricted production in the United States between 1935 and 1939, world trade in lard declined very sharply, and partially recovered only with the resumption of large-scale shipments from the United States to England in about 1940 In the period 1925–1929, the average annual world trade in lard amounted to about 855,000,000 pounds, of which 731,000,000 pounds represented exports from the United States[6] In 1937, world trade had declined to about 300,000,000 pounds, of which 136,000,000 pounds were exported from the United States.

Lard appears on the market in a number of different grades, according to the part of the animal from which it is derived and the method employed in rendering it The production and consumption of the various grades of lard in the United States will be discussed in more detail in a later chapter (page 202) devoted to the subject of plastic shortening agents.

(b) *Greases*

A considerable quantity of hog fat which is inedible for one reason or another is marketed as grease In the United States an average of about 5 pounds of grease is produced for each hog slaughtered Grease from hogs is produced in three different grades, namely white, yellow and brown, according to its color, free fatty acid content and general quality.

Although grease is ordinarily considered to be hog fat, and tallow is considered to be the fat of cattle and sheep, the commercial distinction between greases and tallows is made entirely upon the basis of the titer of the fat[8] Consequently, packing house greases may in some cases contain minor amounts of fats from animals other than hogs

There are a number of low-grade greases which may or may not consist largely of hog fat These include bone grease, which is derived from the processing of bones for gelatine, glue, etc , tankage grease, a low-grade fat extracted from animal residues, house grease, which is the waste fat from restaurants and hotels, and garbage grease, which is recovered from collections of city garbage

The production of the various greases in the United States is indicated in Table 36

TABLE 36

FACTORY PRODUCTION IN MILLION POUNDS OF ANIMAL FATS IN THE U S IN 1941[a]

Edible fats		Yellow grease	126 2
Lard	1537 4	Brown grease	97 4
Rendered pork fat	155 6	Lard oil[b]	51 8
Tallow	91 1	Bone grease	31 8
Oleostearine	46 0	Tankage grease	49 4
Oleo oil	92 2	House grease	40 6
TOTAL, edible fats	*1922 3*	Garbage and other grease	31 8
		Tallow oil	10 4
Inedible fats		Neatsfoot oil	4 3
Tallow	821 0	TOTAL, inedible fats	*1387 9*
White grease	123 2	GRAND TOTAL, all animal fats	*3310 2*

[a] U S Bur Census, *Animal and Vegetable Fats and Oils* Washington, 1942
[b] Partially edible

(c) *Tallow and Tallow Derivatives*

Tallow may be the fat of either cattle or sheep There is no great difference between the two fats, and ordinary packing house tallow, while consisting largely of beef fat, may contain a small proportion of mutton tallow Inedible tallows may contain hog fat[8] In packing houses in the United States, the average yield of beef tallow and tallow products from each animal slaughtered is in the neighborhood of 80 pounds.

The United States is the largest producer of tallow, with a production in 1941 of 821,000,000 pounds of inedible tallow, and approximately 230,000,000 pounds of edible tallow and tallow derivatives[9] In Germany an average of about 170,000,000 pounds of tallow were produced annually in the years 1932–1936[7] In 1934 the total estimated production of tallow and tallow products in the United Kingdom was about 75,000,000 pounds[7]

Australia, New Zealand, Argentina, and Uruguay are all large producers and exporters of tallow Statistics on the production of tallow in these

[8] A fat with a titer below 40°C is considered a grease, a fat with a titer over 40°C is considered a tallow

[9] U S Bur Census, *Animal and Vegetable Fats and Oils* Washington, 1942

countries are not available, but in 1935 exports from these countries were respectively, 51, 57, 103, and 38 million pounds[7] The United Kingdom, the United States, Germany, and the Netherlands are normally the chief importing countries

Much the greater part of the United States production of tallow consists of inedible products which are used in the production of soaps There are a number of different grades of inedible tallow on the market As in the case of the greases, grading of tallows is carried out on the basis of their color (which is judged as such or after a standard bleaching test) and their content of free fatty acids

TABLE 37

AVERAGE PRICES IN CENTS PER POUND OF VARIOUS ANIMAL FATS IN THE U S

(In barrels or tierces, including the cost of the container, all prices at Chicago, except for oleostearine, at New York)[a]

Year	Lard P S	Tallow edible	Oleo oil extra	Oleostearine	Tallow No 1 inedible	Grease A white
1929	11 5	8 9	10 9	10 5	8 0	8 0
1930	10 4	6 8	10 5	8 9	5 6	5 6
1931	7 7	4 6	6 3	7 6	3 4	3 5
1932	4 6	3 5	5 6	5 2	2 7	2 6
1933	5 3	3 7	5 9	5 0	3 0	3 0
1934	7 7	5 0	7 6	6 9	3 8	4 0
1935	13 8	8 6	12 2	10 8	6 2	6 8
1936	11 3	7 8	10 4	9 0	5 8	6 3
1937	11 3	8 6	12 4	9 7	7 5	8 0
1938	8 0	6 1	8 8	7 2	5 0	5 3
1939	6 4	5 5	8 0	6 8	5 1	5 2
1940	5 4	4 6	7 1	6 0	4 1	4 2
1941	8 9	7 7	9 7	9 0	7 2	7 3
1942[b]	13 8	9 9	13 0	10 5	8 4	8 8

[a] U S Dept Agr, *Agricultural Statistics* Washington R M Walsh U S Dept Agr B A E *private communications* A Dewees, *U S Dept Agr Statistical Bull* No 59 (1937)

[b] Government controlled prices prevailing at the close of the year

A large part of the production of edible tallow consists of so called oleo stock, which is fractionally crystallized and pressed to yield oleo oil and oleostearine

Neatsfoot oil is a special inedible product which is rendered from the feet of cattle

Inedible tallows and greases are consumed almost entirely in the manufacture of soaps A considerable part of these soaps are used in the manu facture of lubricating greases rather than as detergents In 1940 the consumption of inedible tallow and greases in soaps and miscellaneous products (principally lubricants) was 1,043 000 000 and 196,000,000 pounds, respectively, in the United States[10]

[10] U S Tariff Commission *Fats Oils and Oil Bearing Materials in the United States* Washington 1941

Although grease is ordinarily considered to be hog fat, and tallow is considered to be the fat of cattle and sheep, the commercial distinction between greases and tallows is made entirely upon the basis of the titer of the fat[8] Consequently, packing house greases may in some cases contain minor amounts of fats from animals other than hogs

There are a number of low-grade greases which may or may not consist largely of hog fat These include bone grease, which is derived from the processing of bones for gelatine, glue, etc , tankage grease, a low-grade fat extracted from animal residues, house grease, which is the waste fat from restaurants and hotels, and garbage grease, which is recovered from collections of city garbage

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Australia, New Zealand, Argentina, and Uruguay are all large producers and exporters of tallow Statistics on the production of tallow in these

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[9] U S Bur Census, *Animal and Vegetable Fats and Oils* Washington, 1942

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1930	10 4	6 8	10 5	8 9	5 6	5 6
1931	7 7	4 6	6 3	7 6	3 4	3 5
1932	4 6	3 5	5 6	5 2	2 7	2 6
1933	5 3	3 7	5 9	5 0	3 0	3 0
1934	7 7	5 0	7 6	6 9	3 8	4 0
1935	13 8	8 6	12 2	10 8	6 2	6 8
1936	11 3	7 8	10 4	9 0	5 8	6 3
1937	11 3	8 6	12 4	9 7	7 5	8 0
1938	8 0	6 1	8 8	7 2	5 0	5 3
1939	6 4	5 5	8 0	6 8	5 1	5 2
1940	5 4	4 6	7 1	6 0	4 1	4 2
1941	8 9	7 7	9 7	9 0	7 2	7 3
1942[b]	13 8	9 9	13 0	10 5	8 4	8 8

[a] U S Dept Agr *Agricultural Statistics* Washington R M Walsh, U S Dept Agr, B A E, *private communications* A Dewees, *U S Dept Agr*, *Statistical Bull* No 59 (1937)

[b] Government controlled prices prevailing at the close of the year

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[10] U S Tariff Commission *Fats Oils and Oil Bearing Materials in the United States* Washington 1941

5. Oleic-Linoleic Acid Oils

(a) Cottonseed Oil

Cottonseed oil is obtained from the seeds of various species of the plant *Gossypium* The oil is a by-product of the growing of the plant for fiber The world's greatest cotton-producing region is the southern United States; other important producing countries are India, China, Russia, Egypt, and Brazil

In the United States, about 900 pounds of cottonseed will ordinarily be produced to each 500-pound bale of cotton lint or fiber The average yields

TABLE 38
WORLD PRODUCTION OF COTTONSEED IN 1936–1937[a]

Country	Seed, thousand tons	Oil equivalent million pounds
United States	5,540	1,720
India	2,890	895
China	2 180	675
Russia	1,830	567
Brazil	1,030	319
Egypt	915	284
Mexico	175	54
Uganda	158	49
Peru	157	49
Turkey	138	43
Anglo Egyptian Sudan	134	42
Other countries	655	203
TOTAL	15,802	4,900

[a] Imperial Economic Committee, *Vegetable Oils and Oilseeds* H M Stationery Office, London, 1938.

of the various products resulting from the processing of one short ton of cleaned seeds are approximately as follows

Linters	143 pounds, or 7 15%
Hulls	520 pounds, or 26 0%
Oil cake	906 pounds, or 45 3%
Crude oil	312 pounds, or 15 6%
Loss (principally moisture)	120 pounds, or 6 0%

The average yields of cottonseed and cottonseed oil per acre in the United States in the period 1938 to 1942 were 458 pounds and 72 pounds, respectively [11] Under exceptional conditions, yields in small areas may be twice as great or greater

In the season of 1936–1937 the world production of cottonseed, in terms of short tons of seed and their equivalent in oil (on the basis of an oil yield of 15 5%), was as indicated in Table 38 The actual yield of oil from these quantities of seed can only be guessed In the United States, 1,364,000,000 pounds of crude oil were realized from 5,540 tons of seed, or about 79% of a potential production of 1,720,000,000 pounds [6] This may be con-

[11] Private communications from R M Walsh, U S Dept Agr, B.A E

sidered a maximum yield, however In such countries as China and India, the percentage of the total crop crushed is probably less, and the yield of oil per ton of seed lower

International trade in both cottonseed and cottonseed oil is relatively small In past years, the trade in cottonseed has consisted largely of imports to Great Britain from Africa and Brazil Trade in cottonseed oil

TABLE 39

PRODUCTION IN MILLION POUNDS OF COTTONSEED SOYBEAN AND PEANUT OILS IN THE U S[a]

Year	Cottonseed	Soybean	Peanut
1931–1932	1 694	40	12
1932 1933	1 446	29	15
1933–1934	1 303	26	10
1934 1935	1 109	78	56
1935–1936	1 164	209	64
1936–1937	1 364	184	78
1937 1938	1 961	279	67
1938–1939	1 409	416	85
1939 1940	1 325	533	33
1940 1941	1 425	564	174
1941–1942	1 250	707	76

[a] U S Dept Agr *Agricultural Statistics* Washington (1943 and preceding years)

TABLE 40

FACTORY CONSUMPTION IN MILLION POUNDS OF COTTONSEED OIL IN THE U S IN DIFFERENT EDIBLE PRODUCTS[a]

Year	Shortening	Margarine	Other edible products[b]
1931	928 5	16 0	84 4
1932	834 4	15 1	100 1
1933	852 8	18 0	121 6
1934	1 058 7	54 8	155 3
1935	991 8	99 5	138 6
1936	918 9	108 1	178 3
1937	1 162 6	173 6	226 6
1938	1 051 3	142 9	198 2
1939	905 0	98 7	233 4
1940	*823 4*	*115 9*	*263 3*

[a] U S Tariff Commission *Fats Oils and Oil Bearing Materials in the United States* Washington 1941

[b] Chiefly salad and cooking oils

has been light and has largely consisted of shipments from Brazil to the United States In 1937 imports of cottonseed into all of the importing countries amounted to approximately 978 000 short tons, equivalent to about 150 000 000 pounds of oil[7] Of this amount approximately 78% was imported by the United Kingdom

For many years the production of cottonseed oil in the United States far outranked that of all other vegetable oils Lately, however, cottonseed oil has much decreased in relative importance in this country, due to very large increases in the production of soybean and peanut oils (see Table 39)

Cottonseed oil is very little used for any purpose except the manufacture of edible products The small quantity consumed in soaps (about 6% of the total) consists almost entirely of oil in the *form of foots*, which are derived from the alkali refining of the oil for edible purposes Practically no cottonseed oil is used in making paints, etc

The average price of cottonseed oil during different years in the United States is shown in Table 41

TABLE 41
PRICE IN CENTS PER POUND OF COTTONSEED OIL IN THE U S [a]

Year	Crude tanks S E mills	Refined, P S Y tanks New York	Year	Crude tanks S E mills	Refined, P S Y tanks New York
1929	8 08	9 71	1936	8 6	9 8
1930	6 86	8 18	1937	8 0	9 2
1931	5 29	6 14	1938	6 7	7 9
1932	3 10	3 83	1939	5 6	6 6
1933	3 66	4 53	1940	5 3	6 2
1934	5 57	6 50	1941	9 5	10 5
1935	9 22	10 42	1942	12 75[b]	13 95[b]

years)
A ..

(b) *Peanut Oil*

Peanut oil, otherwise known as arachis, earth nut, or ground nut oil, is a product of the seeds of the plant, *Arachis hypogaea* The culture of peanuts is successful only in reasonably warm climates Large quantities are grown for consumption as food, in addition to those grown for oil production There is in general little difference between the nuts used for oil and those used for other edible products, although the varieties yielding very large kernels are somewhat preferred for the latter purpose In the United States the Spanish and Runner varieties are both crushed for oil and shelled for the edible trade, *whereas the large kernelled* Virginia variety is used almost wholly as an edible nut Peanuts are raised for the production of oil throughout the southern United States, with the state of Georgia being the largest individual producer

In the past, peanut oil has been principally obtained from nuts grown in India and Africa and exported to Europe for crushing Most of the peanuts imported into Europe are crushed for their oil In the United States the peanuts processed for oil amounted to one-fourth or less of the total crop prior to 1940 The estimated production of peanuts in the principal producing countries of the world in 1936, in terms of unshelled weight in short tons, is shown in Table 42 In recent years the growing of peanuts for oil in the United States has increased considerably *In the season of* 1940-1941, of a total production of 1,540,000,000 pounds, 558,000,000 pounds were crushed, to yield 171,000,000 pounds of crude oil [6]

The oil content of peanuts is quite variable, but whole nuts will generally yield about 30% oil and shelled nuts will generally produce 45–50% oil. In the southeastern United States average yields per ton of whole nuts in

TABLE 42
WORLD PRODUCTION OF PEANUTS IN THOUSAND SHORT TONS IN 1936[a]

India	3,040	Belgian Congo (in 1933)	121
China	2,900	Kwantung	87
Senegal	665	Argentina	80
United States	650	Gambia	63[b]
Nigeria	265[b]	Formosa	61
Netherlands East Indies	262	Spain (in 1935)	24
Burma	159	Other African countries (in 1935)	235
French Sudan	148	TOTAL	8,760

[a] Imperial Economic Committee, *Vegetable Oils and Oilseeds*. H. M. Stationery Office, London, 1938.
[b] Exports.

TABLE 43
INTERNATIONAL TRADE IN PEANUTS IN 1938[a]

Country	Net exports, million pounds	Net imports, million pounds
British India	2,016	—
Senegal	1,194	—
Nigeria	605	—
Manchuria	245	—
China	163	—
Gambia	105	—
Portuguese Guinea	70	—
Netherlands Indies	68	—
Mozambique	42	—
Other African countries	44	—
France	—	2,375
United Kingdom	—	1,087
Germany	—	1,025
Netherlands	—	558
Belgium	—	274
Italy	—	175
Japan	—	103
Denmark	—	102
Union of South Africa	—	56

[a] U. S. Dept. Agr., *Agricultural Statistics*, Washington.

milling peanuts of the Spanish and Runner types are approximately as follows:

Oil	600–625 pounds, or 30–31%
Cake (45% proteins)	900–925 pounds, or 45–46%
Hulls	300–320 pounds, or 15–16%
Loss	160–200 pounds, or 8–10%

Peanuts yield a relatively large amount of oil per acre, as compared with most other annual oil seed crops. In the five year period 1938–1942 the average yield of peanut oil per acre in the United States was 216 pounds.[11]

The average yield of peanuts (which were not all processed for oil) per acre during the same period was 741 pounds Under favorable conditions yields may in some localities be considerably greater

Peanut oil is used for the same purposes as cottonseed oil, in fact, it may be considered interchangeable with the latter oil for all except a very few purposes The one field in which much cottonseed oil is consumed, to the exclusion of peanut oil, is the manufacture of winterized salad oils

The average price of peanut oil during different years in the United States, is indicated in Table 44

(c) *Olive Oil*

Olive oil is derived from the fruit coat of olives, from the tree, *Olea europea* The cultivation of olive trees apparently originated in the Mediterranean area, and the world's supply of olive oil still comes almost entirely from the countries bordering the Mediterranean sea

TABLE 44

PRICE OF PEANUT OIL IN THE U S (TANK CARS, S E MILLS)[a]

Year	Cents per pound	Year	Cents per pound
1930	7 2	1936	8 8
1931	5 6	1937	8 4
1932	3 4	1938	6 9
1933	4 0	1939	5 9
1934	6 0	1940	5 7
1935	9 5	1941	9 7
		1942	13 00[b]

[a] U S Dept Agr, *Agricultural Statistics*, Washington R M Walsh U S Dept Agr B A E *private communications* A Dewees, *U S Dept Agr Statistical Bull* No 59 (1937)

[b] Government controlled price prevailing at the end of the year

The world production of olive oil varies a great deal from season to season, according to the weather, but averages close to two billion pounds yearly In the season of 1932-1933, which may be regarded as more or less average, the production of olive oil in the principal producing countries was as shown in Table 45 In the United States the major portion of the olive crop is usually consumed as a food rather than being crushed for oil In the years between 1930 and 1942 from 26 62% of the total crop was crushed, with the production of 664,000 to 10,331,000 pounds of oil

Most of the olive oil is consumed in the countries of production, ordinarily less than one fourth of the total production enters international trade Normally, the United States is the largest importer and Spain is the largest exporter of oil A considerable proportion of the olive oil exported consists of low grade or inedible oil, which is consumed in various industrial applications rather than as a food Of 126,000,000 pounds of olive oil imported into the United States in 1935, 18,000,000 pounds consisted of

of inedible, denatured oil and 34,000,000 pounds consisted of olive "foots"

The yield of oil from the fruit and the yields of olives and oil per [illegible] are extremely variable, but the statistics relative to production in Sp[illegible]

TABLE 45

WORLD PRODUCTION OF OLIVE OIL IN MILLION POUNDS IN 1932-1933[a]

Spain	769	Turkey	80
Italy	463	Algeria	30
Greece	296	French Morocco	21
Tunisia	121	France	19
Portugal	86	Approximate world production	1935

[a] International Institute of Agriculture *Oils and Fats Production and Inter[illegible] tional Trade* Rome, 1939

TABLE 46

INTERNATIONAL TRADE IN OLIVE OIL IN MILLION POUNDS (1935)[a]

Country	Net exports	Net imports	Country	Net exports	Ne[illegible] impo[illegible]
Spain	139	—	United States	—	126
Tunisia	110	—	Argentina	—	48
Algeria	68	—	France	—	4
Greece	25	—	United Kingdom	—	2
Turkey	15	—	Cuba	—	20
Syria and Lebanon	14	—	Italy	—	1[illegible]

[a] International Institute of Agriculture *Oils and Fats Production and Inter[illegible] tional Trade* Rome, 1939

TABLE 47

AVERAGE PRICES IN CENTS PER POUND OF DIFFERENT GRADES OF OLIVE OIL IN THE U S[a]

In drums, New York

Year	Ed ble	Ined ble	Foots	Year	Ed ble	Ined ble	Foo[illegible]
1935	23 1	11 4	8 6	1939	26 3	12 9	7 8
1936	24 1	13 3	8 7	1940	32 0	19 6	9 0
1937	31 9	19 4	11 1	1941	62 5	45 1	15 1
1938	26 0	12 9	8 0	1942[b]	58 4	51 2	19 0

[a] U S Dept Agr , *Agricultural Statistics* Washington (1943 and preceding yea[illegible]

[b] Average price prevailing during the month of December

in the season of 1935-1936[12] give some indication of the average yields obtained In this season 2,250,000 metric tons or 4,960,000,000 pou[illegible] of olives were produced from 1,921 000 hectares or 4,745,000 acres

[12] International Institute of Agriculture, *Oils and Fats Production and In[illegible] national Trade* Rome 1939

It is impossible to estimate what proportion of the above total was actually crushed for the production of oil

Since 1936 the cultivation of sunflowers in Argentina has increased greatly In 1942, 1,461,000,000 pounds of seed were crushed to yield 385,500,000 pounds of oil Up to 1941, international trade in this commodity consisted of small and sporadic exports of oil from Russia In 1941 Argentina entered the world trade with exports of 26,000,000 pounds of oil, and in 1942, exports from that country amounted to 130,900,000 pounds of oil, in addition to 77,000,000 pounds of seeds

Sunflowerseed oil is principally used for edible purposes It has only mild drying properties, is quite stable, is not subject to flavor reversion, and is little, if any, inferior to cottonseed oil as a raw material for the manufacture of salad and cooking oils, shortening, and margarine In the United States, crude sunflower seed oil is usually quoted at a price slightly in excess of that of cottonseed oil

(f) Sesame Oil

Sesame oil is a product of the seeds of the annual plant, *Sesamum indicum,* which is grown principally in India and the warmer regions of China The seeds are used both for food and for the production of oil

In China, where the cultivation of sesame is carried out most successfully, the average yield of seed per acre appears to be in the neighborhood of 550 pounds Somewhat smaller average yields are obtained in India and most of the other producing countries The average yield of oil from crushing the seed is approximately 47%

The production of sesame seed in the principal growing countries in 1936 was (in million pounds) approximately [12]

China	1910
India	1073
Turkey	88
Anglo Egyptian Sudan	68
Mexico	55
Other countries	206
TOTAL	3400

The probable percentage of the above crushed for oil is unknown

International trade in both sesame seed and sesame oil is small The total exports of seed in 1936 were 350,000,000 pounds, of which 235,000,000 pounds were from China [13] The chief importers in 1936 were the United States, 109,000,000 pounds, Japan, 53,000,000 pounds, and Italy and the Netherlands, about 28,000,000 pounds each International trade in sesame oil has always been small and has consisted largely of oil crushed in Denmark and the Netherlands from imported seed

[13] Imperial Economic Committee, *Vegetable Oils and Oilseeds* H M Stationery Office, London, 1938

Sesame oil is used for a variety of purposes in the Orient, but in the United States and probably also in Europe it is consumed almost exclusively in edible products In the United States it has in the past commanded a slight premium over cottonseed and other domestically produced oils

(g) *Corn Oil*

Corn or maize oil, which is derived from the seeds of the plant, *Zea mays*, is a by-product of the corn starch and grain alcohol industries It is expressed from the germ of the seed, which is separated from the remainder of the kernel by the wet milling process when the latter is prepared for the manufacture of starch or glucose There is also a small production of corn oil from germs separated by dry milling The germ (wet process) contains 40–50% of oil, about 1 25 pounds of oil being obtained from each bushel of corn

TABLE 50
PRODUCTION OF CORN OIL IN MILLION POUNDS IN THE U S [a]

Year	Corn milled by the wet process (1000 bu)	Corn oil produced by the wet milling industry[b]	Total production of corn oil crude basis
1932	61,760	111 6	—
1933	75 118	118 4	—
1934	65,850	129 5	—
1935	58,319	109 3	—
1936	74,497	125 3	—
1937	68 402	133 0	127 5
1938	73,322	129 2	136 7
1939	77,244	135 3	150 6
1940	81 710	159 7	158 1
1941	110,293	167 3	203 4

[a] U S Dept Agr, *Agricultural Statistics*, Washington (1943 and preceding years) U S Bur Census, *Animal and Vegetable Fats and Oils*, Washington, 1942
[b] Total of crude and refined oil sold by the industry

Most of the corn oil is produced in the United States, although there is a limited production in some of the European countries Certain data relative to the production of corn oil in the United States in recent years are listed in Table 50

In the United States, corn oil is used practically exclusively for the manufacture of salad and cooking oils Corn oil is usually quoted at a price closely corresponding to that of cottonseed oil The government controlled price prevailing at the close of 1942 was 12 75 cents per pound for the crude oil, in tanks at the mills

(h) *Minor Oleic-Linoleic Acid Oils*

Kapok oil, like cottonseed oil, is a by-product of fiber production. The kapok tree, *Eriodendron anfractuosum*, is chiefly grown in the Netherlands

As soybeans are relatively low in oil content, the yield of oil obtained from them depends to a considerable extent upon the method used for its extraction In the United States the average yield of oil by expression in screw presses or expellers is considered to be about 9 pounds per 60 pound bushel, or 15% By hydraulic pressing the average yield is a little smaller (*ca* 8 pounds), but solvent extraction produces about 11 pounds per bushel, or 18 3% The solvent extraction process is used to a much greater extent on soybeans than on any other oil seed There is no important difference between solvent extracted and mechanically expressed oil

TABLE 54

WORLD PRODUCTION OF SOYBEANS IN 1936[a]

Country	Million pounds	Country	Million pounds
China	13,000	Japan	748
Manchuria	9,190	Other Far Eastern countries	593
United States	1 795	Russia	233
Korea	1 070	European countries	98

[a] International Institute of Agriculture, *Oils and Fats Production and International Trade* Rome, 1939

TABLE 55

INTERNATIONAL TRADE IN SOYBEANS IN MILLION POUNDS (1937)[a]

Country	Exports	Imports	Country	Exports	Imports
Manchuria	4350	—	Germany	—	1324
Korea	343	—	Denmark	—	542
Other countries	179	—	Sweden	—	258
Japan	—	1670	Netherlands	—	220

[a] Imperial Economic Committee, *Vegetable Oils and Oilseeds* H M Stationery Office London 1938

Since a comparatively large residue of oil cake is left after expression of the oil, this cake is a relatively valuable product of the crushing process At the prices usually prevailing in the United States, its value is approximately equal to that of the oil

The yield of soybeans in the United States averages about 17 to 18 bushels per acre

In the past, exports of soybeans have been almost entirely from Manchuria, where the crop is largely grown for export Exports from China are negligible Prior to 1939 approximately one-third of the Manchurian crop went to Japan, while most of the remainder was exported to Europe. International trade in soybeans in the principal exporting and importing countries in 1937 is shown in Table 55.

Unlike the other linolenic acid oils, soybean oil is used primarily as an edible oil and only secondarily as a material for the manufacture of paints, etc The amount of soybean oil consumed in different classes of products in factories in the United States in 1940 was (in million pounds)[14]

Edible products	392
Soap (in the form of oil)	18
Soap (in the form of foots)	26
Paint, varnish, etc	43
Miscellaneous	19

The average price of soybean oil in the United States in different years is shown in Table 56

(b) *Linseed Oil*

Linseed oil is produced from the seeds of the flax plant, *Linum usitatissimum* Except in certain portions of Europe and Russia, the varieties of flax cultivated for seed are not utilized in the production of fiber The raising of flax for seed is principally carried on in countries like Argentina, Russia, the United States, and Canada, where wide areas of relatively new land are still available The cultivation of flax is not adapted to regions of intensive agriculture In the United States most of the flaxseed production is from the states of Minnesota and North and South Dakota

In the period 1938–1942 the average yield of flaxseed in the United States was 521 pounds per acre In Argentina yields are somewhat higher, averaging in some years as high as 720 pounds per acre The yield of oil from flaxseed is about 34%

The world production of flaxseed in 1936 in million pounds was[12]

Argentine	4270
Russia	1700
India	868
United States	295
Uruguay	169
Canada	102
Other European countries	562
Other countries	67
TOTAL	8033

In the United States the flaxseed crop is extremely variable, ranging in recent years from a high of 1,760 000,000 pounds in 1924 to a low, in 1936, of 295,000 000 pounds[15]

International trade in flaxseed is large since the greater part of the seed grown in Argentina, India and Uruguay is exported The exports and imports of flaxseed in the principal trading countries in 1938 are shown in Table 57

[15] U S Dept Agr *Agricultural Statistics* Washington (1943 and preceding years).

In certain countries, particularly in Russia, considerable quantities of linseed oil are consumed as an edible oil In the United States practically the entire consumption of linseed oil is in paints, linoleum, printing inks and other industrial products requiring an oil with good drying properties

Average wholesale prices of raw linseed oil in the United States during different years are shown in Table 58

TABLE 56
PRICE OF SOYBEAN OIL IN THE U S
(Crude oil in tank cars at the mills)[a]

Year	Cents/lb	Year	Cents/lb
1930	8 6	1937	8 1
1931	5 5	1938	5 6
1932	3 1	1939	4 8
1933	5 4	1940	4 7
1934	6 0	1941	8 5
1935	8 1	1942	11 8[b]
1936	7 5		

[a] U S Dept Agr *Agricultural Statistics* Washington (1943 and preceding years) A Dewees *U S Dept Agr*, *Statistical Bull* No 59 Washington, 1937
[b] Government controlled price prevailing at the end of the year

TABLE 57
INTERNATIONAL TRADE IN FLAXSEED IN 1938[a]

Country	Exports million pounds	Imports million pounds
Argentina	2790	—
India	642	—
Uruguay	160	—
Lithuania	125	—
United States	—	860
Netherlands	—	657
United Kingdom	—	620
France	—	448
Germany	—	342
Belgium	—	188
Italy	—	116

[a] International Institute of Agriculture *Oils and Fats Production and International Trade* Rome, 1939

(c) *Minor Linolenic Acid Oils*

Perilla oil is a product of the seeds of the plant, *Perilla ocymoides*, which is cultivated in various countries of the Far-East, and particularly in Manchuria The average yield of oil from perilla seed is about 37%[14] The yield of oil per acre of cultivated plants appears to be comparable to that from flax

Most of the perilla oil produced has in the past been consumed in the United States In 1935 imports of perilla oil into this country reached a maximum of 114,000,000 pounds In succeeding years, however, imports

which is extracted from its flowers Recently, small amounts of safflower seed have been grown in the southwestern United States The oil is quite similar to high iodine value soybean oil, and presumably can be used for the same purposes

Walnut oil is derived from the seed kernels of the common English walnut, *Juglans regia*, which is cultivated principally in Central Europe, Asia Minor and the United States Relatively few walnut kernels are pressed for oil but the oil is particularly adapted to the manufacture of artist's colors and other fine paints, because of its lack of tendency to yellow with age, and hence is of some slight commercial importance

Candlenut or lumbang oil is obtained from the seeds of the tree, *Aleurites moluccana*, which grows wild throughout the islands of the Pacific, including Hawaii and the Philippines In its drying properties it is quite similar to linseed oil Candlenut oil is not produced in large quantity, but finds some local use in soaps and paints

Chiaseed oil is obtained from the annual plant, *Salvia hispanica*, which grows both wild and cultivated in Mexico As three crops per year may be harvested in that country, the yield of seed per year under proper cultivaln is said to be quite high, amounting to as much as a ton per acre The yield of oil from the seed is about 33% There is little chiaseed oil on the market, however, the seed are principally utilized in the production of a beverage The oil is similar to perilla oil in its properties

Cedarnut oil is derived from the seed of the evergreen tree, *Pinus cembra*, which grows wild in great numbers in Europe, and more particularly in western Russia and Siberia Large quantities of this oil are said to be potentially available, but no data are available as to its actual production

8 Conjugated Acid Oils

(a) *Tung Oil*

Tung oil or Chinawood oil is produced from the seed kernels of the tree, *Aleurites fordii* Some of the oil exported from China is apparently derived from the closely related *Aleurites montana* The oil from the two trees is virtually identical

The tung tree requires a subtropical climate It is a native of Southern China, and most of the oil commercially produced comes from China and adjacent countries, but smaller plantings have been made in other regions, including South American and the southern United States

Yields of tung oil are in the neighborhood of 16% on the basis of the whole fruit, 35% on the basis of the whole kernels, and 55% on the basis of the separated kernels The productiveness of the trees appears to vary widely Plantations of the United States produce about 300 pounds of oil per acre in successful seasons Apparently somewhat higher yields are obtained in some of the Chinese provinces [16] The trees bear in about

their fourth or fifth year, reach a maximum productiveness in about 10 years, and continue to bear up to an age of about 30 years

In the past almost the whole of the world's tung oil supplies have come from China, although small quantities are produced in the United States, Russia, Argentina and Brazil In 1942, 16,400,000 pounds of nuts were crushed in the United States, to yield 5,200,000 pounds of oil The United States production, while extremely variable, is believed to be greater than

TABLE 60
PRICE OF TUNG OIL IN THE U S
(Drums, New York)[a]

Year	Cents/lb	Year	Cents/lb
1929	14 6	1936	16 1
1930	9 6	1937	15 7
1931	7 4	1938	13 5
1932	6 3	1939	21 0
1933	6 8	1940	26 3
1934	8 9	1941	32 2
1935	17 0	1942	39 0[b]

years)

A

that of any other country except China In 1936, the exports of Chinese oil to the various importing countries was (in million pounds) [16]

United States	137 0
Hong Kong (largely for re export)	13 3
Germany	9 5
United Kingdom	8 3
France	8 1
Netherlands	3 6
Japan	2 2
Other countries	9 0
TOTAL	191 0

Tung oil is used only as a drying oil, chiefly in the manufacture of varnishes and similar finishes It is superior to ordinary oil for varnish manufacture because of its rapid drying properties and its high resistance to moisture The oil cake remaining after the extraction of the oil is poisonous and, unlike most oil cakes, is unsuitable for stock feeding

The price of tung oil in the United States has increased rapidly since 1938, due to the growing demand for fast drying finishes and difficulties in obtaining shipments of the oil from China The average prices of tung oil during recent years are shown in Table 60

(b) *Oiticica Oil*

Oiticica oil is expressed from the seed kernels of the tree, *Licania rigida,* which grows wild in Brazil, chiefly in the state of Ceara There is a closely

related tree (*Licania arborea*) found in Mexico which yields an oil (cacahuanache oil) similar to the Brazilian oil As yet, however, the oil from this tree has not appeared on the market in any quantity

The crop of oiticica seeds is extremely variable from year to year The adult tree is said to yield about 330 pounds of seeds per year,[17] and to come into full bearing at an age of about 10 years The life of the tree is estimated as 100 years Unlike the babassu and other palm seed, the oiticica seed may be cracked and the kernel extracted without difficulty The seeds consist of about 60% kernels, which in turn yield about 60% oil.

TABLE 61

BRAZILIAN PRODUCTION AND EXPORTS OF OITICICA OIL DURING 1936-1941[a]

Year	Production million pounds	Exports million pounds	Exports to U S million pounds
1936	13 9	7 3	4 2
1937	4 6	3 4	2 5
1938	35 7	8 2	6 8
1939	7 0	20 5	18 9
1940	22 1	16 0	15 4
1941	—	36 5	36 5

[a] Brazilian Ministry of Foreign Affairs, Brazil, *An Economic Social and Geographic Survey*, Rio de Janeiro, 1941 U S Vegetable Oil Mission to Brazil, Report, Washington, 1942

TABLE 62

PRICE OF OITICICA OIL IN THE U S

(Drums, New York)[a]

Year	Cents/lb	Year	Cents/lb
1935	16 3	1939	15 0
1936	12 6	1940	18 9
1937	12 9	1941	20 2
1938	11 1	1942	25 0[b]

[a] U S Dept Agr , *Agricultural Statistics*, Washington (1943 and preceding years)
[b] Government controlled price at the end of the year

All crushing of the seed for oil is carried out in Brazil, as the exportation of seed is forbidden by law The United States has consumed practically the entire output of oiticica oil since the latter first assumed important proportions

Oiticica oil, like tung oil, is used only as a drying oil, the two oils are quite similar in their properties

Average prices prevailing for oiticica oil in the United States in recent years are shown in Table 62

[17] Brazilian Ministry of Foreign Affairs, Brazil, *An Economic, Social and Geographic Survey* Rio de Janeiro, 1941

9. Marine Oils

(a) Whale Oil

Whale oil forms an important item of commerce in Europe In the season of 1936–1937 the world's production of whale oil, distributed according to the countries of registration of the whaling vessels, was (in million pounds) [16]

Norway	444
United Kingdom	390
Union of South Africa	90
Japan	72
Panama	67
United States	56
Denmark	29
Germany	22
Other countries	30
TOTAL	1200

Most of the whale oil production is from the Antarctic region The total number of whales taken during the season was 51,256, indicating a yield of oil per whale of about 23,500 pounds Yields in preceding years were generally higher, ranging up to 32,000 pounds Imports of whale oil into the different countries in 1936 in million pounds were [16]

Germany	358
United Kingdom	340
Netherlands	146
Denmark	103
Norway	96
United States	29
Poland	18
France	2

The imports listed in this table do not include those of Japan

Although whale oil is an oil of higher quality than any of the fish oils, and is more suitable for edible purposes, it must nevertheless be regarded as a substitute for the more desirable land animal and vegetable fats The price of whale oil is generally lower than that of any of the other fats or oils, with the exception of the fish oils and the inedible tallows and greases

The principal use for whale oil in Europe is in the manufacture of margarine and other edible fat products Large quantities are also consumed in the manufacture of soaps Practically all of the whale oil is hydrogenated before it is consumed

(b) Fish Oils

The fish oils which are of the greatest commercial importance are sardine, menhaden, and herring oils

The largest producer of fish oils is the United States, which in the period 1934–1938 had an average yearly output of 222,000,000 pounds, consisting for the greater part of sardine oil from fish taken off the Pacific coast Under normal circumstances, the second largest producer of fish oils is probably Norway The Norwegian production of herring oil in 1936 was 60,000,000 pounds, of which 26,000,000 pounds was exported[16] In the

TABLE 63

FACTORY UTILIZATION OF FISH AND FISH LIVER OILS IN THE U S IN 1940[a]

Class of use	Million pounds
Edible products (shortening)	11
Soap	89
Paints	46
Miscellaneous	34

[a] U S Tariff Commission, *Fats Oils, and Oil Bearing Materials in the United States* Washington, 1941

TABLE 64

AVERAGE PRICES IN CENTS PER POUND OF FISH OILS IN THE U S DURING SPECIFIED YEARS (CRUDE OIL)[a]

Year	Sardine tanks Pacific coast	Menhaden tanks Baltimore	Herring tanks Pacific coast
1929	6 1	6 2	5 3
1930	4 4	4 6	—
1931	3 0	2 7	3 0
1932	1 9	1 9	2 1
1933	2 2	1 8	2 2
1934	2 7	2 6	2 3
1935	4 6	4 0	4 1
1936	4 5	4 3	—
1937	6 0	5 2	—
1938	4 7	4 4	—
1939	4 1	4 0	—
1940	4 9	4 2	—
1941	7 4	6 8	—
1942[b]	8 9	8 8	8 9

[a] U S Dept Agr , *Agricultural Statistics*,"
A Dewees *U S Dept Agr Statistical Bu*
[b] Prices for sardine and menhaden oils ar
government established ceiling price

same year, Norway also exported 41,000,000 pounds of other fish oils Japan is also a large producer of fish oils Figures are not available on the total Japanese production, but exports in 1936 amounted to 81,000,000 pounds

Fish oils are used for a variety of purposes where a cheap fat is desired For the manufacture of edible products or soaps it is invariably hydrogenated The 180,000,000 pounds of fish oil consumed in the United

States in 1940 was divided amongst the various classes of uses as shown in Table 63.

(c) *Fish Liver Oils*

Fish liver oils are important as medicinal oils and for the preparation of vitamin concentrates, because of their high content of vitamins A and D.

The most important fish liver oil is cod liver oil, of which Norway has in the past been the chief source of supply. In 1936 the Norwegian production of fish liver oils amounted to 24,000,000 pounds.[16] In 1935 the production of fish liver oils in the United States was only 1,750,000 pounds, but it has since increased greatly, partly from an augmented production of cod liver oil, and partly from the utilization of a wide variety of other fish, not previously taken for their liver oils.

The consumption of cod liver oil in the United States was 45,000,000 pounds in 1940. Of this, 6,000,000 pounds was of domestic origin and 39,000,000 pounds was imported.[18]

10. Hydroxy Acid Oils

Castor Oil

Castor oil is extracted from the seeds or "beans" of the plant, *Ricinus communis*, which is a perennial in the tropics, but an annual in those regions which are visited by frost. The yield of oil from the seed is variable, according to the variety of seed, but is usually between 40% and 45%.

The castor plant grows chiefly in India, Manchuria, Russia, and Brazil. Reliable data on the production of castor beans in the different countries are not available. However, as the oil is not edible and is used mainly for industrial purposes, and as industrial requirements for castor oil are not extensive in any of the producing countries except Russia, the international trade in castor beans is a good indication of the extent to which the oil is produced and utilized in different countries. In 1937 international trade in castor beans was as follows (in million pounds):[16]

Country	Exports	Imports
Brazil	264	—
India	119	—
Manchuria	60	—
Other countries	29	—
United States	—	148
Japan	—	92
United Kingdom	—	72
France	—	40
Italy	—	36
Belgium	—	22

The period since 1937 has been marked by a greatly increased demand for castor oil in the United States, principally for the manufacture of dehy-

[18] U. S. Tariff Commission, *Fats, Oils, and Oil-Bearing Materials in the United States*. Washington, 1941.

drated castor oil, and an increased production in Brazil, where many of the plants grow in a wild or semiwild condition The 1939 and 1940 castor bean crops in Brazil amounted to approximately 278 and 330 million pounds, respectively, and exports of beans from Brazil were 489,000,000 pounds in 1941 In 1940 the United States imported 238,000,000 pounds of beans, of which 163,000,000 pounds came from Brazil and 72,000,000 pounds from India International trade in castor oil has always been small, amounting to but 45,000,000 pounds in 1937 Trade in oil between the United States and Brazil is negligible

Because of its unique chemical composition, castor oil is particularly suitable for a variety of industrial uses At the present time its major use is in the production of dehydrated oil for the manufacture of paints and varnishes It is also extensively used in lubricants and in fluids for hydraulic systems Large quantities are sulfonated, for use in the textile industry It has long been used for medicinal purposes It is not edible, nor is the residue remaining after extraction of the oil suitable for animal feeding Of the 90,000,000 pounds of castor oil used in the United States in 1940, 2,000 000 were reported used in soaps, 41,000,000 were used in paints, varnishes, etc , and 47,000,000 were used in miscellaneous manufactured products [18]

Price quotations on castor oil in New York, November 1942, were as follows (cents per pound) No 3 grade, barrels—13 8, No 1 grade, tanks—13 0, and dehydrated, drums—18 6

CHAPTER VII

COMPOSITION AND CHARACTERISTICS OF THE INDIVIDUAL FATS AND OILS[1]

1 The Milk Fats

(a) Butterfat (from Cows' Milk)

Butterfat is distinguished by the great variety of its component fatty acids While the general composition of butterfat has long been known,[2] a number of the minor acids have been identified only recently, and in some cases doubt still exists as to the occurrence of specific fatty acids

Butterfat contains all the saturated fatty acids, from butyric to stearic, as well as a small proportion (0 5–2 0%) of higher molecular weight fatty acids, which are usually reported as arachidic However, Bosworth and Sisson,[3] who carefully examined the high molecular weight fraction of the methyl esters from a very large sample of butter, were unable to detect arachidic acid, finding in this fraction only stearic and behenic acids

Since butterfat yields no insoluble addition products upon bromination it was long assumed that its unsaturated acids consisted solely of oleic acid This assumption has been shown to be in error, careful examination of the unsaturated C_{18} acids of butterfat has revealed the presence of diethenoid acids with double bonds in the same position as in ordinary linoleic acid from vegetable oils [4] The thiocyanogen absorption of butterfat also indicates the presence of a diethenoid acid Thus, for example, 41 samples of butterfat examined by Andrews and Richardson[5] contained 1 4 to 4 8% of linoleic acid as calculated from iodine and thiocyanogen values The diethenoid C_{18} (octadecadienoic) acid present in butterfat is generally believed to be a geometric isomer of the linoleic acid occurring in vegetable oils [6]

In addition to ordinary oleic acid, recent analyses of butterfat have shown it to contain small amounts of decenoic, dodecenoic tetradecenoic, and

[1] GENERAL REFERENCES T P Hilditch *The Chemical Constitution of Natural Fats* Wiley New York 1941 G S Jamieson *Vegetable Fats and Oils* 2nd ed Reinhold N [illegible]
F [illegible]

[3] A W Bosworth and E W Sisson *J Biol Chem* 107, 489–496 (1934)
[4] [illegible] 29 1564–1576 (1935)
[5] [illegible] 90–94 (1943)
[6] [illegible]

hexadecenoic acids [7, 10] In the older analyses of butterfat, these acids are generally neglected, being reported as oleic acid

The presence of highly unsaturated C_{20} and C_{22} acids in butterfat was observed first by Bosworth and Brown,[7] and again by Bosworth and Sisson,[3] who noted the specific presence of arachidonic acid Acids of this type occur in the fat, however, only in traces

Traces of a dihydroxystearic acid in butterfat were reported by Browne,[2] and Bosworth and Helz[11] isolated traces of a liquid, optically active hydroxy palmitic acid

Representative analyses of butterfat in terms of its fatty acid composition are given in Table 65, which also contains certain other analytical data and the only reported estimate of the composition of this fat in terms of its component glycerides, by Hilditch and Sleightholme [12] In comparing the different analyses, the limitations of the older analyses, as mentioned above, are to be recalled It may also be mentioned that butter produced in the United States will often be somewhat lower in iodine value than any of the English butters in this table The iodine value of American butter is frequently as low as 25 to 30

The composition of butterfat is considerably influenced by the feed of the cow It has often been noted that the iodine value of butterfat will average 5 to 8 units higher in the summer, when the cows are on pasturage, than in the winter when they are stall fed The inclusion of specific oils in the feed of the animals is inclined to affect the composition of the saturated rather than the unsaturated portion of the fatty acids [12, 13] Thus, feeding cotton seed meal will lower the iodine value of the butter, due to the approximately 25% of saturated acids in cottonseed oil, in spite of the fact that this oil contains about 25% and 50%, respectively, of oleic and linoleic acids The feeding of highly unsaturated vegetable oils does not produce in the butterfat linolenic acid or the form of linoleic acid present in vegetable oils However, if cows are fed fish oil there is a marked increase in the amount of highly unsaturated C_{20} and C_{22} acids, with a corresponding reduction in the amount of lower unsaturated acids [13] The effect of different rations on the composition and characteristics of butterfat will be discussed at greater length in a subsequent chapter on butter and margarine (pages 246–272)

There is also considerable variation in the butterfat produced by different

[7] A W Bosworth and J B Brown, *J Biol Chem* **103**, 115–134 (1933)

[8] T P Hilditch and H Paul *Biochem J*, **30**, 1905–1914 (1936)

[9] H E Longenecker, *J Soc Chem Ind* **56**, 199–202T (1937)

[10] T P Hilditch and H E Longenecker *J Biol Chem*, **122**, 497–506 (1937)

[11] A W Bosworth and G E Helz *J Biol Chem* **112**, 489–492 (1936)

[12] T P Hilditch and J J Sleightholme *Biochem J*, **24**, 1098–1113 (1930), **25**, 507–522 (1931)

[13] T P Hilditch and H M Thompson, *Biochem J*, **30**, 677–691 (1936)

Table 65

Composition (in Per Cent by Weight) and Certain Characteristics of Butterfat

Analysis	Hilditch and Sleightholme[a]	Hilditch and Sleightholme[a]	Hilditch and Sleightholme[a]	Hilditch and Longenecker[b]	Hilditch and Jasperson[c]	Hilditch and Jasperson[c]
Characteristics						
Iodine value	31 6	34 8	41 6	37 5	37 5	42 9
Saponification equiv	242 7	243 3	248 2	248 0	247 7	251 8
Refractive index at 60°C	1 4450	1 4455	1 4473	—	—	—
Reichert-Meissl value	29 3	32 3	25 7	—	26 1	27 4
Polenske value	3 2	2 0	2 2	—	1 85	1 78
Kirschner value	23 7	25 5	20 6	—	21 8	21 8
Composition of fatty acids						
Butyric	3 4	3 6	3 3	3 0	3 6	3 7
Caproic	2 0	1 5	1 3	1 4	2 0	1 7
Caprylic	1 1	1.7	1 2	1 5	0 5	1 0
Capric	3 2	3 8	2 2	2 7	2 3	1 9
Lauric	7 3	6 5	4 0	3 7	2 5	2 8
Myristic	17 1	10 6	10 4	12 1	11 1	8 1
Palmitic	27 0	26 3	26 1	25 3	29 0	25 9
Stearic	4 8	8 3	6 5	9 2	9 2	11 2
Arachidic	—	1 2	—	1 3	2 4	1 2
Decenoic	—	—	—	0 3	0 1	0 1
Dodecenoic	—	—	—	0 4	0 1	0 2
Tetradecenoic	—	—	—	1 6	0 9	0 6
Hexadecenoic	—	—	—	4 0	4 6	3 4
Oleic	31 7	32 9	40 9	29 6	26 7	32 8
Octadecadienoic	2 4	3 6	4 1	3 6	3 6	3 7
C_{20} & C_{22} unsat	—	—	—	0 3	1 4	1 7
Composition of glycerides						
Trisaturated	41 3	38 2	27 2	—	—	—
Disaturated monounsaturated	33 9–46 3	34 0–47 9	33 0–52 9	—	—	—
Monosaturated diunsaturated	24 8–0	27 8–0	39 8–0	—	—	—
Triunsaturated	0–12 4	0–13 9	0–19 9	—	—	—

[a] T P Hilditch and J J Sleightholme, *Biochem J*, 24, 1098–1113 (1930), 25, 507–522 (1931)
[b] T P Hilditch and H E Longenecker, *J Biol Chem*, 122, 497–506 (1937)
[c] T P Hilditch and H Jasperson, *J Soc Chem Ind*, 60, 305–310 (1941)

Table 66

Distinctive Characteristics of Butterfat in Comparison with Other Fats and Oils

Analysis	Butterfat	Coconut oil	Palm kernel oil	Ordinary fats and oils
Saponification value	210–235	245–260	240–250	Below 200
Refractive index at 60°C	*ca* 1 4465	*ca* 1 4410	*ca* 1 4430	Over 1 4500[a]
Reichert-Meissl value	22–34	6–8	5–7	<1
Polenske value	2–4	14–18	10–12	<1
Kirschner value	20–26	1–2	0 5–1	<0 5

[a] Provided the iodine value is not below about 50

animals on identical rations Dean and Hilditch[14] observed a decline in the proportion of palmitic acid with advancing age in milk cows, and there are also variations in the butterfat according to the duration of the period of lactation

Butterfat is distinguished from other oils except those of the lauric acid group by the low average molecular weight of its fatty acids, (manifested in a high saponification value and a low refractive index), and from coconut oil and other lauric acid oils by its high content of steam volatile acids, as indicated by a high Reichert-Meissl value In addition to the characteristics mentioned above, other average characteristics of butterfat are approximately as follows density at 60°C, 0 887, melting point, 38°C, titer, 34°C, unsaponifiable matter, 0 4%

From the standpoint of the nutritional value of the product, the vitamin A content of butter is important Since the source of the vitamin A in butter is the β carotene or other carotenoid pigments in the feed of the cows,

TABLE 67

VITAMIN A POTENCY OF WISCONSIN BUTTER DURING DIFFERENT MONTHS OF THE YEAR (ON BASIS OF WHOLE BUTTER)[a]

Month	Average vitamin A content μg/g	Average carotene content μg/g	Calculated vitamin A potency I U/lb[b]
March	5 61	2 16	9,568
July	8 96	7 43	17,738
September	9 06	7 66	18,032
January	5 89	2 97	10 488

[a] S Berl and W H Peterson *J Nutrition*, **26**, 527–538 (1943)

[b] Calculated on the basis 1 I U = 0 6 μg β carotene = 0 25 μg vitamin A

the content of this vitamin varies considerably, being highest in the summer when the dairy herds are on pasture, and lowest in the winter when there are no green feedstuffs in their rations A portion of the carotene in the feed is transferred to the butterfat without change The amount of carotene ingested by the cow into the butterfat exhibits a variation with the feeding regime parallel to variations in the production of vitamin A, so that the depth of yellow color in the butter serves to some extent to indicate its vitamin A content

Actually, the entire vitamin A potency of butter is in part due to vitamin A as such, and in part due to carotene, which is partially coverted to the vitamin in the human body The relative biological activities of vitamin A and carotene can hardly be regarded as settled One International Unit of vitamin A is defined as the amount possessing the biological activity of 0 6 μg of pure β carotene The biological activity of pure vitamin A was

[14] H K Dean and T P Hilditch, *Biochem J*, **27**, 889–897 (1933)

for some time considered to be about 3,000,000 I U per gram However, the most recent work[15] has indicated that the activity of this vitamin, either as such or in the form of its esters, is in the neighborhood of 4,000,000 I U per gram On this basis the vitamin A potency of butter would be expressed by the following equation.

$$\text{I U} = 4\ 0 S + 1\ 67 C$$

where I U = International Units per gram, S = vitamin A content in μg per gram, and C = carotene content in μg per gram As the result of extensive tests in which a number of samples of butter were biologically assayed for vitamin A potency and also tested for carotene and vitamin A content by chemical methods, Fraps, Kemmerer, and Meinke[16] some time ago proposed the following alternative formulas (the second formula being preferred)

$$\text{I U} = 3\ 2 S + 1\ 7 C$$

$$\text{or I U} = 4\ (S - 0\ 5) + 1\ 7 C$$

A recent investigation of vitamin A in butter is that of Berl and Peterson,[17] who conducted chemical assays for both this vitamin and carotene on large numbers of samples representative of the Wisconsin butter production during different months of the year The data of these investigators are summarized in Table 67 It will be seen that carotene contributes only from 15–25% of the vitamin A potency of the butter These results are in accord with the earlier work of Baumann and Steenbock[18] which had indicated that carotene accounted for no more than 15% of the vitamin A activity of butter

Different breeds of cows on the same rations produce butters differing significantly in both vitamin A and carotene content Shorthorn cows produce relatively pale butters which are low in carotene content, but not correspondingly low in vitamin A Guernsey cows produce butterfat which is high in carotene and strongly colored, but not particularly high in content of vitamin A Holstein cows have been found to be outstanding in the high vitamin A content of their butterfat, particularly in the winter

Carotene and vitamin A contents of butterfat from winter and summer butters of different breeds of cows, as reported by two different groups of observers, are listed in Table 68 In this table, the results of Baumann *et al*[19] represent tests made on American butters, while those of Gillam

[15] J G Baxter and C D Robeson *J Am Chem Soc*, **64**, 2411–2416 (1942) K Hickman, *Ann Rev Biochem* **12**, 353–396 (1943)

[16] G S Fraps A R Kemmerer, and W W Meinke, *J Assoc Official Agr Chem*, **24**, 731–735 (1941)

[17] S Berl and W H Peterson, *J Nutrition*, **26**, 527–538 (1943)

[18] C A Baumann and H Steenbock, *J Biol Chem*, **101**, 547–560 (1933)

[19] C A Baumann, H Steenbock, W M, Beeson, and I W Rupel, *J Biol Chem*, **105**, 167–176 (1934)

et al [20] and Booth *et al* [21] are from the examination of English butters The somewhat higher values for vitamin A reported by the former group may be attributed in part to the use of a different method of calculating contents of this vitamin from spectrophotometric data, and probably do not represent real differences in the two varieties of butter

The vitamin D content of butter is much less significant than that of vitamin A, but is nevertheless appreciable It varies from about 0 1 to 1 0 I U per gram, being highest in the summer, and lowest in the winter

TABLE 68

CAROTENE AND VITAMIN A CONTENTS OF BUTTERFAT FROM DIFFERENT BREEDS OF COWS ON SUMMER AND WINTER RATIONS

(Content in μg per g dry fat)

Season and breed	Baumann Steenbock Beeson and Rupel[a]		Gillam Heilbron Ferguson and Watson[b]		Booth Kon and Gillam[c]	
	Carotene	Vitamin A	Carotene	Vitamin A	Carotene	Vitamin A
SUMMER						
Ayrshire	5 5	12 2	4 1	11 8	—	—
Brown Swiss	9 8	13 8	—	—	—	—
Friesian	—	—	4 7	12 1	—	—
Guernsey	17 0	18 5	11 4	9 5	22 4	8 9
Holstein	6 6	15 1	—	—	—	—
Jersey	10 7	11 5	—	—	—	—
Shorthorn	—	—	2 9	8 4	7 8	11 0
WINTER						
Ayrshire	4 8	8 4	2 7	6 6	—	—
Brown Swiss	6 0	7 8	—	—	—	—
Friesian	—	—	3 5	6 1	—	—
Guernsey	10 3	6 8	7 3	5 4	5 0	3 4
Holstein	5 2	10 2	—	—	—	—
Jersey	7 1	7 1	—	—	—	—
Shorthorn	—	—	2 5	5 8	1 9	3 9

[a] C A Baumann, H Steenbock, W M Beeson, and I W Rupel, *J Biol Chem*, 105, 167-176 (1934)

[b] A E Gillam I M Heilbron, W S Ferguson and S J Watson, *Biochem J*, 30, 1728-1734 (1936)

[c] R G Booth, S K Kon, and A E Gillam, *Biochem J* 28, 2169 2174 (1934)

(b) *Other Milk Fats*

The milk fat of other grazing animals is very similar, in composition and characteristics, to the milk fat of cows Analyses of milk fats from various animals other than the cow are contained in Table 69 In connection with miscellaneous milk fats it may be mentioned that Indian ghee may legally be composed of fat derived from the milk of cows, buffaloes, goats or sheep, or any mixture of these fats It is to be noted that the milk fats of goats and sheep are distinguished from cow butterfat by their higher Polenske

[20] A E Gillam, I M Heilbron, W S Ferguson, and S J Watson, *Biochem J*, 30, 1728-1734 (1936)

[21] R G Booth, S K Kon, and A E Gillam, *Biochem J*, 28, 2169-2174 (1934)

values and lower Kirschner values, but are virtually indistinguishable from each other

Goat butter is characteristically very pale in color, due to a low carotene content, but is not correspondingly low in vitamin A Typical carotene and vitamin A contents of summer goat butter, as reported by Gillam and Heilbron,[22] are 0 21 and 4 1 μg per gram, respectively

TABLE 69
COMPOSITION (IN PER CENT BY WEIGHT) AND CHARACTERISTICS OF MISCELLANEOUS MILK FATS

Analysis	American goat milk[a]	Indian goat milk[b]	Sheep milk[b]	Camel milk[c]	Buffalo milk[d]
Composition of fatty acids					
Butyric	2 1	3 0	3 3	2 1	4 1
Caproic	1 9	2 3	2 8	0 9	1 4
Caprylic	2 7	3 9	3 8	0 6	0 9
Capric	7 9	8 6	7 8	1 4	1 7
Lauric	3 5	4 6	5 4	4 6	2 8
Myristic	10 2	11 5	12 2	7 3	10 1
Palmitic	28 7	24 7	23 5	29 3	31 1
Stearic	8 1	9 3	6 9	11 1	11 2
C_{20}, C_{22}, C_{24} satd	0 4	0 1	1 9	—	0 9
Decenoic	0 2	—	—	—	—
Tetradecenoic	0 4	—	—	—	—
Hexadecenoic	2 1	—	—	—	—
Oleic	31 2	30 5	28 3	38 9	33 2
Linoleic	—	1 5	4 1	3 8	2 6
C_{20}, C_{22} unsatd	0 7	—	—	—	—
	—	28 8	32 1	40 8	33 5
	—	238 1	232 4	259 0	—
	—	235	242	217	—
	—	1 4523	1 4526	1 4555	—
	—	0 44	0 45	0 24	—
Reichert Meissl value	—	31 7	33 9	16 4	—
Polenske value	—	8 2	8 0	1 6	—
Kirschner value	—	19 0–16 8	15 8 21 0	14 3	—

[a] R W Riemenschneider and N R Ellis *J Biol Chem* **113,** 219 233 (1936)
[b] D R Dhingra *Biochem J*, **27,** 851 859 (1933)
[c] D R Dhingra *Biochem J* **28,** 73–78 (1934)
[d] R Bhattacharya and T P Hilditch, *Analyst* **56,** 161 170 (1931)

2 The Lauric Acid Oils

(a) *Coconut Oil*

Most of the characteristics which distinguish coconut oil and other lauric acid oils from ordinary oils may be traced to a high content of low molecular weight fatty acids Although referred to as an oil, coconut oil may be solidified at ordinary atmospheric temperature, having a melting

[22] A E, Gillam and I M Heilbron *Biochem J* **28,** 1082 1085 (1934)

point in the neighborhood of 76°F (24.4°C). Its low melting point is not due to a relatively high degree of unsaturation, as in the case of ordinary oils, but rather is due to the low molecular weight of its glycerides.

Unlike most fats, both natural and hydrogenated, coconut oil does not exhibit a gradual softening with increasing temperature but is inclined to pass rather abruptly from a brittle solid to a liquid, within a temperature range of a relatively few degrees. The reason for this peculiarity of coconut oil is readily apparent from consideration of its composition.

In order for a fat to melt and soften gradually, and thus exhibit an extended plastic range, it must be composed of a mixture of low melting and high melting glycerides. While the melting points of the glycerides are determined by the manner in which the fatty acids are grouped within the glycerides, a wide range of melting in the glycerides is nevertheless dependent upon there being a corresponding range in the melting points of the component fatty acids. Coconut oil contains a greater variety of fatty acids than most oils, but this variety is occasioned by differences in the molecular weights of saturated acids, rather than by differences in the degree of unsaturation of the acids. Normally, about 75% of the total fatty acids of coconut oil consist of lauric, myristic, and palmitic acids. These acids melt at approximately 44°, 54°, and 63°C., respectively, hence there is a difference of but 19° between the melting points of the lowest and the highest members. On the other hand, the major fatty acids of high molecular weight fats are usually linoleic, oleic, palmitic and stearic acids, which melt at −7°, 16°, 63°, and 70°C., with a difference of 77° between the lowest and the highest melting of the group. The relatively narrow melting range of the coconut oil fatty acids is reflected in the glycerides, and accounts for the limited plastic range of the latter.

Also unlike ordinary oils, coconut oil can be changed but little in melting point and consistency by hydrogenation. Even complete hydrogenation serves only to convert approximately 9% of combined oleic and linoleic acids to stearic acid, the saturated acids comprising 91% of the oil are of course unaffected by the process. Completely hydrogenated coconut oil has a melting point of about 111°F (45.1°C). The narrow plastic range of coconut oil and the inability of the processor to modify greatly the physical properties of the oil by hydrogenation severely restrict the use of this oil in edible products. Coconut oil is seldom used as a major ingredient in shortening, and its short plastic range is even undesirable in margarine, although here the disadvantage is less, since the consistency of margarine is to some extent patterned after that of butter. Butter also has a comparatively short plastic range, due in part to the fact that it likewise contains a large proportion of low molecular weight fatty acids.

Since its unsaturation is low, coconut oil is extremely resistant to the development of rancidity. However, free acids are very noticeable in

a coconut oil product if present in considerable amount, since they sufficiently volatile and soluble to contribute a decided odor and fla

Crude coconut oil usually comes upon the market with a somewhat hig free fatty acid content than ordinary vegetable seed oils According to trading rules commonly used in the United States the highest grade of c nut oil is required only to have a free acid content (calculated as oleic a under 3%, and much crude oil is as high as 5% in free acids Coconut derived from copra of good quality is very light in color, the crude oil of being not darker than 15 yellow, 1 5 red, on the Lovibond scale In a tion to being low in pigments, coconut oil is very nearly free of phosp tides, gums, and other nonglyceride substances commonly present in from seeds of annual plants

TABLE 70
FATTY ACID COMPOSITION OF COCONUT AND PALM KERNEL OILS IN PER CE BY WEIGHT

Fatty acid	Coconut[a] oil	Coconut[b] oil	Coconut[c] oil[d]	Palm kernel[e]
Caproic	0 5	0 8	Trace	—
Caprylic	9 0	5 4	7 9	2 7
Capric	6 8	8 4	7 2	7 0
Lauric	46 4	45 4	48 0	46 9
Myristic	18 0	18 0	17 5	14 1
Palmitic	9 0	10 5	9 0	8 8
Stearic	1 0	2 3	2 1	1 3
Arachidic, etc	—	0 4	—	—
Oleic	7 6	7 5	5 7	18 5
Palmitoleic	—	0 4	—	—
Linoleic	1 6	—	2 6	0 7

[a] S Lepkovsky, G V Feskov, and H M Evans, *J Am Chem Soc*, 58, 978- (1936)
[b] [illegible] *J Biol Chem* 130 167–177 (1939)
[c] [illegible] (1928)
[d] [illegible]
[e] [illegible]

The fatty acid composition of coconut oil, as reported by three differe groups of analysts, is shown in Table 70 Collin and Hilditch[23] fou coconut oil to consist of 84% trisaturated glycerides, 12% disaturate monounsaturated glycerides, and 4% monosaturated diunsaturated gly cerides

Coconut oil is distinguished from other fats and oils, except other lau acid oils and butterfat, by the low average molecular weight of its fat acids, as evidenced by a high saponification value, and a low refractr index The percentage of coconut oil in a mixture of coconut oil and tallo or other ordinary fats is usually calculated from the saponification value the mixture Andrews,[24] after examining a large number of samples

[23] G Collin and T P Hilditch, *J Soc Chem Ind*, 47, 261–269T (1928)
[24] J. T R Andrews, *Oil & Soap*, 10, 165 (1933).

coconut oil fatty acids, listed the following average values for characteristics of these acids saponification (neutralization) value, 268, iodine value, 10 1, titer, 23 3°C These correspond to a saponification value and an iodine value of 253 and 9 5, respectively, for the glycerides The content *of unsaponifiable matter in coconut oil is usually 0 1–0 3%, and the average* density of coconut oil is about 0 919 at 25°C and 0 893 at 60°C Values for the refractive index, Reichert Meissl, Polenske, and Kirschner values of coconut oil are given in Table 66

The American Oil Chemists' Society recommended standard[25] for coconut oil is given in Table 71

(b) *Palm Kernel Oil*

Palm kernel oil is very similar to coconut oil in almost every respect It has a somewhat higher iodine value than coconut oil, due to a higher content of unsaturated acids However, the saturated fatty acids in which palm kernel oil is deficient, as compared with coconut oil, are principally the lowest melting members of the series, caproic and caprylic, hence its melting point and titer are but little different from those of coconut oil The fatty acid composition of a typical sample of palm kernel oil is recorded in Table 70 Collin and Hilditch[23] found this sample to contain 63% of trisaturated, 26% of disaturated monounsaturated, and 11% of monosaturated-diunsaturated glycerides

TABLE 71
A O C S STANDARD FOR COCONUT OIL

Specific gravity at 99°/15 5°C	0 869-0 874
at 25°/15 5°C	0 917-0 919
Refractive index at 40°C	1 448 1 450
Iodine value[a]	7 5-10 5
Saponification value[a]	250-264
Unsaponifiable matter %	Not over 0 5
Titer, °C	20-24
Setting point °C	21 8-23
Reichert Meissl value	6-8
Polenske value	15-18

[a] The addition of oils from the paring or rind of the kernel to ' whole ' coconut oil will raise the iodine value to 11 14 and lower the saponification value to 248 254

Iodine values of about 16 to 23 have been recorded for palm kernel oil, the average iodine value of a large number of samples was found by Ellis and Hall[26] to be 18 6 Other average characteristics of palm kernel oil are approximately as follows saponification value, 248, refractive index at 60°C, 1 4430, density at 60°C, 0 892 melting point, 26°C, and unsaponifiable matter, 0 4% The Reichert Meissl, Polenske, and Kirschner values

[25] See *Oil & Soap* 20, 163 164 (1943)
[26] R H Ellis and E M Hall, *J Soc Chem Ind*, 38, 128T (1919)

of palm kernel oil, which are slightly different from those of coconut oil, are listed in Table 66

The A O C S recommended standard for palm kernel oil[25] is as follows

Specific gravity at 99°/15 5°C	0 860-0 873
Refractive index at 40°C	1 449-1 452
Iodine value	14-22
Saponification value	245-255
Unsaponifiable matter, %	Not over 0 8
Melting point, °C	24-26
Setting point, °C	20-26

As in the case of coconut oil, there are no color tests for palm kernel oil, hence it must be detected in admixture with butterfat or other fats and oils

TABLE 72
FATTY ACID COMPOSITION IN PER CENT BY WEIGHT OF AMERICAN PALM KERNEL OILS

Characteristics and composition	Babassu[a]	Babassu[b]	Tucum[c]	Murumuru[d]	Ouricuri[e]	Cohune[f]
Iodine value	16 1	15 1	15 8	11	14 7	9 8
Saponification value	249	—	241	242	256 9	251 0
Caproic	0 2	—	—	—	1 8	Trace
Caprylic	4 8	4 1	1 3	1 1	9 8	7 5
Capric	6 6	7 6	4 4	1 6	8 2	6 6
Lauric	44 1	45 1	48 9	42 5	45 8	46 4
Myristic	15 4	16 5	21 6	36 9	9 0	16 1
Palmitic	8 5	5 8	6 4	4 6	7 7	9 3
Stearic	2 7	5 5	1 7	2 1	2 3	3 3
Arachidic	0 2	0 7	—	—	0 1	—
Oleic	16 1	11 9	13 2	10 8	13 1	9 9
Linoleic	1 4	2 8	2 5	0 4	2 2	0 9

[a] [illegible]
[b] [illegible])
[c] [illegible]
[d] [illegible]
[e] [illegible]
[f] [illegible])28)

through its distinctive refractive index, saponification value, and Reichert Meissl, Polenske, and Kirschner values Its higher iodine value of course differentiates it from coconut oil, although it is virtually impossible to form any reliable estimate of the relative proportions of palm kernel and coconut oil in a mixture of the two

Palm kernels are principally produced in Africa, and shipped to Europe for extraction of the oil Although an effort is made to maintain the free fatty acid content of the kernels at a minimum, by drying the latter before shipment, a considerable time must necessarily elapse between shelling of the kernels and expression of the oil, hence palm kernel oil, like coconut oil, is ordinarily quite high in free fatty acid content

(c) *American Palm Kernel Oils*

The Central and South American palms which have yielded kernel oils in sufficient quantity to be of some commercial importance include the *babassu, tucum, murumuru, ouricuri,* and *cohune*. The composition of samples of these oils, as reported by various observers, are shown in Table 72. All these samples were of American origin except the tucum oil examined by Collin, which was from trees planted in Malaya.

The American palm kernel oils are generally similar to the kernel oil of the African or oil palm. However, tucum and murumuru oils, it is to be noted, are somewhat higher melting than palm kernel oil, and ouricuri oil differs from both coconut and palm kernel oils in its relatively high content of caproic, caprylic, and capric acids, and its correspondingly lower melting point, and higher Reichert-Meissl value. These oils are all similar to coconut and palm kernel oils in free fatty acid content, appearance, plastic

TABLE 73
AVERAGE CHARACTERISTICS OF AMERICAN PALM KERNEL OILS

Analysis	Babassu	Tucum	Murumuru	Ouricuri	Cohune
Iodine value	15.5	9–14	11	15	10–14
Saponification value	247	230–250	242	257	250–255
Density, 60°C	0.893	0.893	0.893	0.898	0.893
Refractive index, 60°C	1.443	1.443	1.445	1.440	1.441
Unsaponifiable matter %	0.2–0.5	0.3	0.3	0.3	0.4
Melting point, °C	22–26	30	32	18	24
Titer, °C	23	27	—	—	21
Reichert-Meissl value	5–7	4	3	6	7
Polenske value	10–12	6	—	18	14

range, etc., and are used for the same purposes. Characteristics of American palm kernel oils are listed in Table 73.

3. The Vegetable Butters

The vegetable butters are the only seed fats which are solid at ordinary temperatures, and are in a number of other respects unique amongst fats and oils. They have the property of melting sharply; in the case of cocoa butter and Borneo tallow, softening and melting occurs over an even more restricted range of temperatures than in lauric acid oils. However, the short plastic range of the vegetable butters is not due to the presence of low molecular weight fatty acids, but arises from the peculiar configuration of the glycerides in these fats. They consist of relatively simple mixtures of glycerides; in some cases they are apparently composed preponderantly of either a single glyceride or of two or more glycerides of very nearly identical melting point. It has been estimated that over 70% of the glycerides of cocoa butter, for example, are composed of a single oleic acid radical in combination with stearic or palmitic acid, or both. Probably about half

of the glycerides of cocoa butter consist of oleo palmito stearin The preponderance of a single glyceride not only causes the fat to melt sharply, but also confers upon it distinctive habits of melting and crystallization Some of the vegetable butters exhibit the phenomenon of polymorphism to a pronounced degree, the consistency and melting point of cocoa butter in particular is variable according to the conditions under which it has been solidified or stored subsequent to solidification

Due to the extensive researches of Hilditch and co workers compositions of the more common vegetable butters are known with considerable exact ness, not only with respect to the component fatty acids, but also with

TABLE 74

COMPOSITION IN PER CENT BY WEIGHT OF SOME VEGETABLE BUTTERS

Analys s	Cocoa butter[a]	Borneo tallow[b]	Shea butter[c]	Mowrah fat (Il pé fat)[d]
Iodine value	36 7	33 2	59 1	63 9
Fatty acids				
Palmitic	24 4	18 0	5 7	23 7
Stearic	35 4	43 3	41 0	19 3
Arachidic	—	1 1	—	—
Oleic	38 1	37 4	49 0	43 3
Linoleic	2 1	0 2	4 3	13 7
Glycerides				
Palmito stearins	2	5	5	1
Monounsaturated palmitostearin	52	31	—	27
Monounsaturated dipalmitin	6	8	—	1
Monounsaturated distearin	19	40	34	—
Diunsaturated stearin	12	13	45	30
Diunsaturated palmitin	9	3	11	41
Triunsaturated			5	—

a

b

c

d

respect to the different classes of glycerides Table 74 contains data on the composition of some of the better known vegetable butters

(a) *Cocoa Butter*

Cocoa butter is a pale yellow solid with the characteristic odor and flavor of the cocoa bean It is brittle at temperatures below about 80°F (26 7°C), slightly above this temperature it softens and melts The melting point of cocoa butter depends upon the crystal modification in which it exists A sample which has been quickly chilled to an unstable crystal form will liquefy if suddenly heated to a temperature as low as 26 30°C However,

if heating is carried out gradually, to permit transformation of the fat to its highest melting form, the melting point will usually be in the neighborhood of 35°C Below its softening point cocoa butter is not greasy to the touch, its combination of hardness and nongreasiness at ordinary temperatures with a melting point below the temperature of the human body make it pre eminently suitable as a coating fat for confections, in which it is ordinarily blended with chocolate Since its characteristic flavor is desirable in confections, cocoa butter is subjected to the processing treatments of refining, deodorization, etc , only when it is desired to reclaim fat whose quality has suffered from age or from damage to the cocoa beans As compared to ordinary fats and oils, cocoa butter is extremely resistant to deterioration through oxidation or the development of rancidity

The composition of a representative sample of cocoa butter is shown in Table 74 Average characteristics of cocoa butter are approximately as follows iodine value, 38, saponification value, 194, refractive index at 60°C, 1 4490, density at 60°C, 0 8825, melting point, 34–35°C , titer, 49°C , unsaponifiable matter, 0 6% Cocoa butter of good quality usually contains 0 5 to 1 0% of free fatty acids

The admixture of foreign fats in cocoa butter will generally be evident from their effect on the consistency of the fat, as determined by micropenetrations or other methods,[27] [28] or from their effect on the turbidity and solidification tests described respectively by Jamieson[29] and Jensen [30] The admixture of lauric acid oils or pressed "stearines" derived from such oils will increase the saponification and Polenske values of the fat It is difficult to determine when cocoa butter has been adulterated with Borneo tallow because of the great similarity between the two fats For the detection of this fat in cocoa butter, the turbidity and solidification tests mentioned above are particularly recommended

Following is the A O C S recommended standard for cocoa butter [31]

Specific gravity at 99°/15°C	0 856–0 864
Refractive index at 40°C	1 453–1 458
Iodine value	35–40
Saponification value	190–200
Unsaponifiable matter %	Not over 1 0
Melting point (open capillary), °C	28–36
Titer °C	45–50

[27] E A Kraemer and A E Bailey, *Oil & Soap* **20**, 235–240 (1943)

[28] R O Feuge and A E Bailey, *Oil & Soap*, **21**, 78–84 (1944)

[29] G S Jamieson, *Vegetable Fats and Oils* 2nd ed , Reinhold, New York, 1943, pp 43–44

[30] H R Jensen *The Chemistry, Flavoring and Manufacture of Chocolate Confectionery and Cocoa* Blakiston Philadelphia, 1931

[31] See *Oil & Soap*, **19**, 140 (1942)

(b) Other Vegetable Butters

Borneo tallow, also known as "green butter," from its characteristic greenish tinge, resembles cocoa butter more closely than any other fat. Published values for its various characteristics vary considerably, and overlap the values given above for cocoa butter. However, it would appear that Borneo tallow may ordinarily be about 5 units lower in iodine value than the average cocoa butter and 2° to 3°C higher in both melting point and titer.

Shea butter is much more unsaturated than cocoa butter or Borneo tallow and is correspondingly softer and less brittle. It is said to be suitable for use as a coating fat only after separation of the more liquid portions by pressing. Shea butter has a characteristically high content of unsaponifiable matter (3–10%). The iodine and saponification values of this fat depend to a great extent upon the amount of unsaponifiable material present. Iodine values of 56 to 65 and saponification values of 178 to 189 are quoted in the literature. The melting point of Shea butter ranges from 33° to 42°C, and the titer from 52° to 53.5°C.

Mowrah fat, or illipé butter resembles Shea butter in being relatively unsaturated, and correspondingly soft. It is said to be used chiefly for candle and soapmaking. A sample of crude fat examined by Hilditch and Ichaporia[32] had an iodine value of 63.9 and a saponification equivalent of 290.2, and contained 2.1% of unsaponifiable matter and approximately 10% of free fatty acids.

Hilditch and Priestman[33] found a sample of *Chinese vegetable tallow* from China to have the following fatty acid composition: lauric, 2.5%, myristic, 3.6%, palmitic, 57.6%, stearic, 1.8%, and oleic, 34.5%. A refined sample of tallow from trees grown in the southern United States was examined at the same time and found to contain the following acids: lauric, 1.2%, myristic, 2.9%, palmitic, 63.1%, stearic, 3.2%, and oleic, 29.6%. The latter sample had an iodine value of 22.1, a saponification equivalent of 275.4 (saponification value, 204), and a setting point of 48.2°C.

Nutmeg butter is characterized by a very high content of myristic acid, the fatty acid composition of this fat, as reported by Collin and Hilditch,[34] being as follows: lauric, 1.5%, myristic, 76.6%, palmitic, 10.1%, oleic, 10.5%, and linoleic, 1.3%. Since nutmeg butter contains a very high proportion of essential oils and other unsaponifiable material, neither the iodine value nor the saponification value are indicative of the composition of the glyceride portion. The original fat examined by the above investigators had an iodine value of 61, and contained 17.7% of unsaponifiable mat-

[32] T. P. Hilditch and M. B. Ichaporia, *J. Soc. Chem. Ind.*, **57**, 44–48T (1938).
[33] T. P. Hilditch and J. Priestman, *J. Soc. Chem. Ind.*, **49**, 397–400T (1930).
[34] G. Collin and T. P. Hilditch, *J. Soc. Chem. Ind.*, **49**, 141–143 (1930); *Biochem. J.*, **23**, 1273–1289 (1929).

ter After the removal of 25% of volatile matter by steam distillation, the residual oil had an iodine value of 46 6 and a saponification equivalent of 295

A sample of refined *ucuhuba butter* from Brazil was examined by Atherton and Meara,[35] who reported the following composition for the fatty acids, Capric acid, 0 5%, lauric acid, 14 8%, myristic acid, 72 5%, palmitic acid, 4 9%, and oleic acid, 6 3% The composition of the glycerides was estimated to be as follows trimyristin, 43%, laurodimyristin, 31%, oleo lauromyristin, 12% and lauromyristopalmitin, 10% The fat had an iodine value of 9 9 and a saponification equivalent of 246 1 (saponification value, 228)

4 The Animal Fats

(a) *Lard*

Lard appears on the market in a number of different grades, according to the part of the animal from which it is derived and the method employed in rendering it The greater portion of the lard produced in the United States consists of *prime steam* lard, which includes fat from all parts of the animal except the leaf fat, and is rendered by a wet method A certain amount of dry rendered lard is also produced, comparable to prime steam lard in composition, but rendered by a dry process *Neutral* lard, wet rendered at a low temperature from selected stock, especially for margarine manufacture, was once an important article of commerce, but has been produced in only small quantity since hydrogenated vegetable and whale oils have become generally available *Leaf* lard is dry rendered from the hard internal fat of the hog and is firmer and lower in iodine value than other lards Small amounts of *kettle rendered* lard other than leaf lard are also produced According to government regulations in the United States, the fat rendered from certain less desirable packing house products may not be called lard, but must be labeled and sold as *rendered pork fat* Rendered pork fat is usually darker in color than lard, and may have a higher free fatty acid content, but is often more resistant to the development of rancidity than ordinary grades of lard

The composition, characteristics, and consistency of lard vary greatly according to the feed of the hogs as well as the part of the animal from which it is taken American prime steam lard has an average iodine value of about 68, the average iodine value of American leaf lard is in the neighborhood of 58 European lard is generally considerably lower in iodine value and firmer than the lard produced in the United States Lard from peanut fed hogs raised in the southern United States is very soft, and often has an iodine value of 85 or more The Oil Characteristics Committee of the

[35] D Atherton and M L Meara, *J Soc Chem Ind*, 58, 353–357 (1939)

A O C S has recommended the following standard for North American lard [31]

Specific gravity at 99°/15 5°C	0 858–0 864
Refractive index at 40°C (Zeiss)	45–52
Iodine value	46 70
Saponification value	195–202
Unsaponifiable matter, %	Not over 1 0
Titer, °C	36–42

Grades Edible Neutral (Nos 1 and 2), Leaf, Choice Kettle Prime Steam
Tests F F A max 1%, peroxide number (milliequivalents) 5 max
Tristearin test for purity
1 Bomer number (ether) not less than 71
2 A O C S (acetone) not less than 73

Since the characteristics of lard will be fully discussed (pages 202 245) in a later chapter devoted to plastic shortening agents, attention here will be directed mainly to certain minor fatty acids of lard, and the glyceride structure of this fat In addition to the stearic and palmitic acids commonly reported, lard contains a small amount (*ca* 1%) of myristic acid An appreciable part of the monoethenoid acids ordinarily reported as oleic acid in lard actually consists of tetradecenoic and hexadecenoic acids Lard also contains small amounts of highly unsaturated C_{20} and C_{22} acids Brown and Deck[36] found as much as 0 4% of arachidonic acid in lard, the total content of unsaturated C_{20} and C_{22} acids is considered by Hilditch[1] to be considerably higher than this The detailed fatty acid analysis of lard from the outer back fat of a hog fed on a low fat diet, as reported by Hilditch, Lea, and Pedelty,[37] is shown in Table 75 This table also contains estimates of the glyceride composition of the same lard, as furnished by Hilditch and Pedelty [38]

The presence of beef fat in lard may be recognized by the Bomer test[39] which is said to depend upon the fact that the palmitodistearin in the two fats is in different forms (*i e*, α and β) However, this test is invalidated by the presence of hydrogenated lards in the fat [40]

(*b*) *Greases*

The term "grease" refers to the softer inedible fats used principally by soapmakers Greases produced by meat packing houses consist almost wholly of inedible lard However, they are defined in terms of their hardness rather than their origin, a fat with a titer below 40°C being considered a grease, and a fat with a titer over 40° being classed as an in

[36] J B Brown and E M Deck, *J Am Chem Soc*, **52**, 1135–1138 (1930)
[37] T P Hilditch C H Lea and W H Pedelty *Biochem J* **33**, 493 504 (1939)
[38] T P Hilditch and W H Pedelty *Biochem J* **34**, 971–979 (1940)
[39] See *Official and Tentative Methods of the American Oil Chemists Society* Revised to Jan 1, 1941, p 44f
[40] L M Tolman and A A Robinson, *Oil & Soap*, **9**, 13 (1932)

edible tallow. Packing house grease is produced in three different grades, white, yellow, and brown, according to the color and free fatty acid content of the material.

White grease is quite similar to lard. In the case of the better grades, its classification as an inedible product may arise chiefly from aesthetic considerations, as it is sterile and may be refined to entire freedom from objectionable impurities, even though it be rendered from inedible materials. The addition of denaturants at the packing houses according to government regulations has served to prevent the diversion of white grease to edible

TABLE 75

COMPOSITION OF LARD (ACCORDING TO HILDITCH, LEA, AND PEDELTY AND HILDITCH AND PEDELTY)

Analysis	Per cent by weight
	59 8
	285.9
	196
	0.2
Fatty acids	
Myristic	1.3
Palmitic	28.3
Stearic	11.9
Tetradecenoic	0 2
Hexadecenoic	2.7
Oleic	47.5
Linoleic (octadecadienoic)	6 0
C_{20} and C_{22} unsaturated	2.1
Glycerides	
Tripalmitin	1
Palmitodistearin	2
Stearodipalmitin	2
Monounsaturated dipalmitin	5
Monounsaturated distearin	—
Monounsaturated palmitostearin	34–27
Palmitodiolein	46–53
Stearodiolein	0–7
Triunsaturated	10–3

uses in the United States, but in the past there have been instances in which white grease has been exported to Europe and illegally refined and sold as a food. *White grease has a red color of less than 2.5 units on the Lovibond scale*, and a free fatty acid content of less than 12%. It is sometimes graded into two or three subgrades, according to free acid content.

Yellow grease is of lower quality than white grease. It is yellowish rather than white in the solidified form, and has a free fatty acid content of from 12 to 25%. *Brown grease* is the lowest grade of packing house grease, being darker in color and higher in free fatty acid content than yellow grease.

There are a number of other greases, which may or may not consist

largely of hog fat These include *bone grease*, which is derived from the processing of bones for gelatin, glue, etc , *tankage grease*, a low grade product extracted from animal wastes, *house grease*, which is the waste cooking fat from restaurants and hotels, and *garbage grease*, which is recovered from collections of city garbage Low grade fats in the grease class are obtained in relatively small amounts from various other sources, such as the degreasing of hides for the manufacture of patent leather and leather upholstery, the disposition of spent tinning and terne plating oils, etc The lower grade greases are in general not used for any industrial purpose as such, but serve as raw materials for the production of distilled fatty acids

Regulations of the U S Department of Agriculture require that white grease or other inedible fats which have the physical properties of edible fats be denatured by the addition of petroleum distillates directly to the vessel in which rendering is carried out

Since greases are principally used in the manufacture of soaps or fatty acids, one of their most important characteristics is their actual content of saponifiable fatty material The nonfatty material in a grease is measured by the so called MIU, which is the combined content of moisture, insoluble impurities, and unsaponifiable matter The MIU figures prominently in the trading rules applied to greases, allowances in the prices of the different grades being made for an MIU above a fixed maximum value

(c) *Tallows and Tallow Derivatives*

Characteristics and compositions of beef, mutton, and goat tallows are recorded in Table 76 The beef tallows with the highest and lowest iodine values represent extremes in the composition of this fat, average packing house tallow in the United States has an iodine value of about 42 The statement has frequently been made that South American tallows are harder and lower in iodine value than North American tallows, because they are derived from grass fed rather than grain fed animals However, in the author's experience there are no consistent differences in either iodine values or firmness amongst edible tallows from the United States, South America, Australia, and New Zealand Certainly the composition of tallow is much less dependent upon the feed of the animals from which it is taken than is lard

Mutton tallow is ordinarily somewhat lower in iodine value than beef tallow, hence the mutton tallow of Table 76 may be regarded as a relatively soft sample Goat tallow is even harder and less unsaturated than mutton tallow The characteristics noted for the Indian goat tallow of Table 76 are all within the range quoted by Pritzker and Jungkunz[41] for Swiss goat tallow The latter authors found this tallow to vary from 32 4 to 38 6 in iodine value

[41] J Pritzker and R Jungkunz *Pharm Acta Helv* , 7, 48 53 (1932)

In addition to the fatty acids reported in the above table, the presence of traces of highly unsaturated C_{20} and C_{22} acids has been reported in beef tallow and mutton tallow, *respectively, by Hilditch and Longenecker*[42] and Hilditch and Zaky[43] In beef and mutton tallows, as in lard, fats derived from the internal tissues of the animals are considerably harder and less unsaturated than those from tissues near the skin Following is the

TABLE 76

CHARACTERISTICS AND FATTY ACID COMPOSITION IN PER CENT BY WEIGHT OF BEEF, MUTTON, AND GOAT TALLOWS

Analysis	Beef[a] (N American)	Beef[a] (S American)	Beef[a] (S American)	Beef[b] (English)	Mutton[c] (English)	*Goat*[d] (Indian)
Iodine value	49 5	42 1	37 1	38 7	41 2	33 5
Saponification equivalent	284 2	280 5	284 0	284 0	285 4	282 0
Saponification value	197	200	197	—	—	
Refractive index at 40°C	—	—	—	—	—	1 4564
Melting point (open tube), °C	42	46	47 5	—	—	—
Setting point, °C	—	—	—	—	—	45 9
Titer, °C	42 3	45 9	47 2	—	—	46 2
Unsaponifiable matter, %	—	—	—	—	—	0 18
Composition, fatty acids						
Lauric	—	—	—	0 5	—	3 5
Myristic	6 3	4 5	7 8	2 7	4 6	2 1
Palmitic	27 4	30 6	27 8	30 4	24 6	25 5
Stearic	14 1	19 1	24 4	23 7	30 5	28 1
Arachidic	—	0 1	—	—	—	2 4
Tetradecenoic	—	—	—	0 4	—	—
Hexadecenoic	—	—	—	1 7	—	—
Oleic	49 6	42 7	38 9	38 6	36 0	38 4
Octadecadienoic	2 5	3 0	1 1	2 0	4 3	—
Composition, glycerides						
Trisaturated	13 9	22 8	25 8	17	26	29 2
Disaturated monounsaturated	22 0–54 1	22 1–49 6	33 7–53 9	49	30–52	30 9 50 9
Monosaturated diunsaturated	64 1–0	55 1–0	40 5–0	34	44–0	39 9–0
Triunsaturated	0–32 0	0–27 6	0–20 3	0	0–22	0–19 9

[illegible]

–50T (1929)
(1938)

standard for beef tallow recommended by the Oil Characteristics Committee of the A O C S [31]

Specific gravity at 99/15 5°C	0 860–0 870
Refractive index at 40°C (Zeiss)	46–49
Iodine value	35–48
Saponification value	193–202

[42] T P Hilditch and H E Longenecker, *Biochem J*, 31, 1805–1819 (1937)
[43] T P Hilditch and Y A H Zaky, *Biochem J*, 35, 940–951 (1941)

Unsaponifiable matter, %	Not over 0 8
Titer, °C	40–46

Grades Edible, Fancy, Choice, Packers Prime, Extra, N Y City Extra and N Y Prod Exchange Contract Grades, Special No 1, No 2, No 3 Western Grades, City, Country Argentine Frigorifico No 1
Based on color, acid, and titer (and MIU)

Only a minor proportion of the total tallow production consists of an edible fat Inedible tallows are marketed in a large number of different grades, according to their color, free fatty acid content, and content of moisture, insoluble impurities, and unsaponifiable matter (MIU content) Edible tallow is classed as such because it is derived from edible materials, rather than because it conforms to definite standards of color, acidity, etc However, edible tallow generally has a light color, similar to that of lard, and a free acid content of less than 1% The better grades of inedible tallow do not have a free fatty acid content of more than 2–3% but are much darker in color than inedible tallow They are bleached without difficulty, however, and may generally be rendered as light as edible tallow by bleaching preceded by alkali refining The poorer grades of inedible tallow are extremely dark in color, and may contain free fatty acids to the extent of 40% or more

Neatsfoot oil is a special inedible product rendered from the feet of cattle It is quite light in color, relatively low in free fatty acid content, and though not highly unsaturated, is sufficiently low in saturated acids to remain liquid at ordinary temperatures Analyses of neatsfoot oil in terms of its component fatty acids, by modern methods, are not available, the following composition was reported by Eckart [44] stearic acid, 2–3%, palmitic acid, 17–18%, oleic acid, 74 5–76 5% The following standard for neatsfoot oil has been recommended by the Oil Characteristics Committee of the A O C S .[31]

Specific gravity at 25°/25°C	0 907–0 912
Refractive index at 25°C	1 464–1 465
Iodine value	66–76
Saponification value	190–199
Unsaponifiable matter, %	Not over 1
Titer, °C	20–30
Pour point (A S T M), °F	20–35

Oleostock is a high grade of inedible tallow prepared by low temperature wet rendering of the fresh internal fat of beef carcasses This fat has a light yellow color, a mild, pleasant flavor, and a free fatty acid content of usually less than 0 2% It generally has an iodine value between about 36 and 40, a titer of 44° to 46°C , and a melting point of about 48°C It is pressed to yield *oleo oil* and *oleostearine*, a hard fat with an iodine value of about 25, and a titer of about 50°C Oleo oil has an iodine value of about

[44] H Eckart, *Z Untersuch Nahru Genussm* , 44, 1–29 (1922), *Chem Umschau Fette Öle Wachse Harze*, 30, 53–56 (1923).

44 to 48, a titer of 41° to 42°C, and melts at about 32° to 34°C (90 94°F), but is quite brittle at refrigerator temperatures Its plastic range is thus very short The free fatty acid contents of oleo stearine and oleo oil are comparable to that of the oleo stock from which they are prepared, but most of the yellow pigments (carotene) of the oleo stock appear in the oil rather than the stearine Oleostearine as it is prepared commercially often contains a sufficient amount of water and water soluble substances remaining from the rendering operation to make it susceptible to deterioration through mold growth

5 The Oleic-Linoleic Acid Oils

(a) *Cottonseed Oil*

Crude cottonseed oil has a strong, characteristic flavor and odor and a dark, reddish brown color from the presence of resinous and other highly colored material extracted from the seed Its free fatty acid content and general quality depend to a considerable extent upon the weather prevailing during the time that the cotton stands in the field after coming to maturity. Hence the quality of crude oil will vary in any given locality from year to year, being highest in dry seasons, and lowest when the seed is exposed to wet weather in the fields, or handled or stored with a high moisture content The free fatty acid content of the best North American oil will vary from 0 5% to 1 0% although oil containing 1 5% to 3 0% of free acids is not uncommon and the free acid content of oil from wet or damaged seeds may be as high as 5% or higher

In the United States, where elaborate trading rules have been evolved for dealing in cottonseed oil, the grade and price of the oil are not established from the characteristics of the crude oil, but are based upon the yield of oil obtained by a standard refining test, and the color of the refined oil The crude oil refines by caustic soda treatment to a relatively light color, *i e*, good oil may readily be refined to a color on the Lovibond scale of 35 yellow and 4 to 7 red As the free fatty acid content of the oil increases, there is a corresponding increase in the refining loss, coupled with a more or less progressive increase in the color of the refined oil Within comparatively wide limits, however, the quality of the refined oil, with respect to its stability, flavor, etc, bears little relation to the free fatty acid content of the crude oil

Cottonseed oil contains more saturated fatty acids than most oils of an equivalent iodine value, hence its titer is high, and the oil itself will become partially solidified upon storage at temperatures below 50° to 60°F Cloud and pour points of refined cottonseed oil by the A S T M method are about 33° to 38°F and 25° to 30°F, respectively [45,46]

[45] A E Bailey R O Feuge, E A Kraemer, and S T Bauer, *Oil & Soap*, **20**, 129-132 (1943)

[46] See *Oil & Soap*, **15**, 245 (1938), **16**, 141 (1939)

Cottonseed oil from the Delta region of the lower Mississippi valley will average very close to 108 in iodine value, seldom being above 111 or below 105 Oil of this iodine value will contain about 25% saturated acids, 25%

TABLE 77
CHARACTERISTICS AND COMPOSITION OF REFINED COTTONSEED OIL FROM DIFFERENT SOURCES

Analysis	U S (Georgia)[a]	U S (Texas)[a]	Sudan (Africa)[a]	Brazil[a]	China[b]
Iodine value	109 2	103 0	101 8	105 5	104 7
Refractive index at 50°C	1 46260	1 46413	1 4636	1 4642	—
Saponification value	194 6	193 0	189 4	192 0	193 0
Acetyl value	9 7	12 0	12 2	11 4	—
Unsaponifiable matter, %	0 54	0 45	0 83	0 77	1 51
Reichert Meissl value	0 45	0 40	0 9	2 0	—
Polenske value	0 53	0 30	0 2	0 4	—
Titer, °C	34 8	32 8	37 0	34 6	31 0
Cloud point (A S T M), °F	30	38	—	—	—
Pour point (A S T M), °F	25	30	—	—	—
Saturated acids	24 0	24 2	27 6	25 6	—
Oleic acid	24 6	27 6	25 4	25 4	—
Linoleic acid	51 4	48 2	46 2	48 2	—

[a] *Oil & Soap*, **15**, 245 (1938), **16**, 141 (1939)
[b] P E Ronzone, *Oil & Soap*, **13**, 165–167 (1936)

TABLE 78
COMPOSITION OF COTTONSEED OIL[a]

Analysis	Per cent by weight
Iodine value	105 0
Saponification equivalent	286 4
Fatty acids	
Myristic	1 4
Palmitic	23 4
Stearic	1 1
Arachidic	1 3
Tetradecenoic	0 1
Hexadecenoic	2 0
Oleic	22 9
Linoleic	47 8
[illegible]	
[illegible]	0 1
[illegible]	5 9
[illegible]	7 3
[illegible]	40 6
[illegible]	17 8
Oleo [illegible]	28 3

[a] T P Hilditch and L Maddison, *J Soc Chem Ind*, **59**, 162 168 (1940)

oleic acid, and 50% linoleic acid, and will have a saponification value of about 195 and a titer of about 34 5°C Texas cottonseed oil is consistently less unsaturated than Delta oil, its iodine value averaging in the neighbor

hood of 103 Cottonseed oil from the southeastern United States is similar in composition to Delta oil Oil from other cotton producing regions of the world appears to generally have characteristics falling within the range

sources are reported in Table 77 A detailed analysis of cottonseed oil, as given by Hilditch and Maddison,[47] including estimates of the minor fatty acids and the glyceride composition, is presented in Table 78

The A O C S recommended standard for refined cottonseed oil[46] is as follows

Specific gravity at 25°/25°C	0 916–0 918
Refractive index at 25°C	1 468–1 472
Iodine value	106–113
Saponification value	190–198
Unsaponifiable matter, %	Not over 1 5
Titer, °C	32 36
Free fatty acids (as oleic) %	Not over 0 25
Clarity	Clear at 70°F for at least 3 hours

South Texas oils, may have an iodine value as low as 99, a titer as low as 30°C, and may not pass the clarity test, due to the separation of solid glycerides

Cottonseed oil is somewhat remarkable for the amount and variety of nonoil substances in the crude oil The content of nonglyceride substances, exclusive of free fatty acids, commonly amounts to 2% or more The following were found by Jamieson and Baughman[48] to be constitutents of the crude oil raffinose pentosans, resins, proteoses, peptones, phosphatides, phytosterols phytosteroline, inosite phosphates, xanthophyll, chlorophyll, mucilaginous substances, and free fatty acids

Cottonseed oil is readily detected in admixture with other oils, even in small amounts, by the well known Halphen color reaction[49] However, the Halphen reaction is destroyed by hydrogenation From the standpoint of its fatty acid composition, cottonseed oil is distinguished by a combination of high saturated acid content with a relatively high iodine value

(b) *Peanut Oil*

Peanut oil, otherwise known as arachis oil, groundnut oil, or earthnut oil, has a rather light yellow color in the crude form, and the characteristic odor and flavor of peanuts As compared with other seed oils, and particu-

[47] T P Hilditch and L Maddison *J Soc Chem Ind*, **59**, 162–168 (1940)
[48] G S Jamieson and W F Baughman, *J Oil & Fat Ind*, **3**, 347 355 (1926)
[49] G S Jamieson *Vegetable Fats and Oils* 2nd ed Reinhold New York 1943

larly cottonseed oil, it is relatively free of phosphatides and other nonoil constituents The oil sold upon the market in the United States usually contains between 0 5% and 1 0% of free fatty acids, but may occasionally be much higher in acidity

Jamieson and Baughman[50] found the oil from a number of samples of Spanish type peanuts grown in the United States to have an average iodine value of 93 7 This appears to be very slightly lower than the average value for oil from the Spanish and Runner varieties cultivated for oil production in this country According to these authors, large kerneled peanuts of the Virginia type, which are principally grown for other uses in the United States, but which are raised for oil in Africa, China, India, etc, produce an oil of approximately the same iodine value as Spanish peanuts, but with a somewhat different fatty acid composition The average saturated acid content of Spanish type peanut oil is about 19% to 20% Oil from the large kerneled variety usually contains 15% to 17% saturated acids

Average characteristics of the refined peanut oil produced in the United States are approximately as follows iodine value, 95, refractive index at 60°C, 1 4558, saponification value, 189, density at 60°C, 0 888, unsaponifiable matter, 0 5%, titer, 31°C

The average peanut oil with the above characteristics will contain about 20% saturated acids, 50% oleic acid, and 30% linoleic acid

The A O C S recommended standard for peanut oil is as follows [51]

Specific gravity at 25°C/25°C	0 910–0 915
Refractive index at 25°C	1 467–1 470
Iodine value	84–100
Saponification value	188–195
Unsaponifiable matter, %	Not over 1 0%
Titer, °C	26–32

The detailed analysis of a sample of peanut oil, as recorded by Hilditch Ichaporia, and Jasperson[52] and Gunde and Hilditch,[53] is shown in Table 79 Recently, the presence of traces of capric and lauric acids in peanut oil was reported [54]

There are no color tests for peanut oil, hence it is most readily detected in other oils through its unusually high content of arachidic, behenic and lignoceric acids Various tests based on the presence of these high molecular weight acids are described in the literature [49] While these tests serve

[50] G S Jamieson and W F Baughman *Cotton Oil Press* 6, No 1 34–35 (1922)
[51] See *Oil & Soap* 18, 194 (1941)
[52] T P Hilditch M B Ichaporia, and H Jasperson *J Soc Chem Ind* 57, 363–368T (1938)
[53] B G Gunde and T P Hilditch *J Soc Chem Ind* 59 47–53 (1940)
[54] H L Wikoff, J M Kaplan and A L Berman *J Biol Chem*, 153, 227 235 (1944)

to indicate qualitatively the presence of considerable amounts of peanut oil in other oils, they do not enable the analyst to detect the presence of minor proportions of other oils in peanut oil, or to estimate with accuracy the relative proportions of peanut oil and other oils in mixtures [55]

Peanut oil, like cottonseed oil, will solidify if exposed to refrigerator temperatures for an extended time The cloud and pour points of peanut oil by the A S T M method are approximately 40° and 34°F [45]

TABLE 79
CHARACTERISTICS AND COMPOSITION IN PER CENT BY WEIGHT OF PEANUT OIL (ACCORDING TO HILDITCH, ICHAPORIA AND JASPERSON AND GUNDE AND HILDITCH)

Iodine value	93 3
Saponification equivalent	295 5
Saponification value	190
Titer, °C	31 8
Unsaponifiable matter, %	0 4
Fatty acids	
Palmitic	8 3
Stearic	3 1
Arachidic	2 4
Behenic	3 1
Lignoceric	1 1
Oleic	56 0
Linoleic	26 0
Glycerides	
[illegible]	1
[illegible]	11
[illegible]	45
[illegible]	24
[illegible]	19

(c) *Olive Oil*

Olive oil has a greenish yellow color, and a characteristic mild, pleasant odor Unlike other vegetable oils, it is consumed as a food without refining, deodorization, or other processing treatment, although in some cases, oil of poor quality may be refined and blended with a better oil Since olive oil is more expensive than other vegetable oils it may on occasion be adulterated with the latter Methods for the detection of various other oils in olive oil will be mentioned under the heading of the individual oils If present in quantity in other vegetable oils, olive oil may be detected though its high content of squalene [56]

Oil which has been extracted from olive press cake by solvents is likewise considered an adulterant in edible oils The detection of extracted and refined oils is discussed at length by Jamieson [49]

[55] See S T Voorhies and S T Bauer, *Oil & Soap*, 20, 175–178 (1943)
[56] J Fitelson, *J Assoc Official Agr Chem*, 26, 499–506 (1943)

Characteristics and compositions of a number of samples of olive oil from different sources are shown in Table 80 It is evident that the proportions of the different fatty acids in olive oil may vary considerably, even in oils with very nearly equal iodine values Iodine values as low as about 75 and as high as about 95 have been reported The titer of olive oil, which is not shown in the table, is about 23°C

The free fatty acid content of olive oil is extremely variable Much of the better oil contains not more than 1-2% of free acids, but oil with a

TABLE 80

COMPOSITION IN PER CENT BY WEIGHT AND CHARACTERISTICS OF OLIVE OIL

Analysis	California[a]	Italy[a]	Spain[a]	Tunisia[a]	Palestine[b]	Italy[c]
Iodine value	85 1	84 4	83 7	86 0	84 0	84 2
Refractive index at 20°C	1 4690	1 4690	1 4689	1 4700	—	—
Saponification value	190 6	190 6	192 4	193 6	191	194
Specific gravity at 25°/25°C	0 9119	0 9120	0 9116	0 9131	—	—
Unsaponifiable matter, %	1 0	1 1	0 8	0 8	1 1	1 3
Acid value	1 5	1 8	1 8	1 9	—	—
Fatty acids						
Myristic	Trace	Trace	Trace	0 1	0 5	1 2
Palmitic	6 9	9 2	9 4	14 4	10 0	15 6
Stearic	2 3	2 0	1 4	2 4	3 3	2 0
Arachidic	0 1	0 2	0 2	0 3	0 1	—
Hexadecenoic	—	—	—	—	—	1 6
Oleic	84 4	83 1	80 5	69 1	77 5	64 6
Linoleic	4 6	3 9	6 9	12 0	8 6	15 0
Glycerides (probable composition)						
Monosaturated diolein	—	—	—	—	45 3	57 2
Monosaturated oleolinolein	—	—	—	—	—	4 2
Linoleo diolein	—	—	—	—	25 5	34 0
Triolein	—	—	—	—	29 2	4 6

[a] G S Jamieson, *Oil & Fat Industries* 4, 63, 426 (1927)
[b] T P Hilditch and H M Thompson *J Soc Chem Ind*, 56, 434–438 (1937)
[c] T P Hilditch and L Maddison *J Soc Chem Ind*, 60, 258 262 (1941)

free fatty acid content up to 5% or higher is not uncommon Pressing of the oil is commonly carried out in two or more stages, with the first pressing yielding the highest grade, so called "virgin" oil, and each successive pressing yielding an oil of lower grade The oils of commerce are commonly blended from a number of stocks of different sources and different grades The residue from the last expression is solvent extracted, usually with carbon disulfide, to produce "sulfur olive oil" or "olive oil foots " This latter product is inedible, it is denatured and sold for the manufacture of soap, and for other industrial purposes

Olive oil is distinctive among vegetable oils for its low iodine value combined with the property of remaining liquid at low temperatures (down

to about 0°C) In this respect, however, it is closely imitated by teaseed oil Due to its low content of linoleic acid, it is more stable toward oxidation than most liquid oils, it is almost completely lacking in drying properties, or any tendency to become gummy when exposed in films Cloud and pour points of olive oil (A S T M method) are about 22° and 14°F, respectively [45]

Standards recommended by the A O C S for edible and inedible olive oils are as follows [57]

Characteristic	Edible	Olive oil foots[b]
[illegible]	0 909–0 915	—
	80 –88	77–90
	188 –196	186–196
	17 –26	16–26
	68 5 –71 6	—
	Not over 1 4	Not over 2 3
	Not over 1 5	—

[a] Minimum I V for California oils shall be 79, maximum I V for African and Dalmatian oils shall be 92

[b] Olive oil foots shall contain not over 3% moisture and insoluble impurities, and not over 0 20% ash

(d) *Palm Oil*

Palm fruits are unavoidably subjected to strong enzyme action during their harvesting and handling prior to expression of the oil, consequently even the better grades of oil are much higher in free fatty acids than most seed oils Oils processed by crude native methods may be hydrolyzed to an extreme degree The value of the oil bears an inverse relation, of course, to its content of free acids

Oils are commercially classified and quoted on the basis of their geographical origin and the free fatty acid content characteristic of oils from each particular locality Sumatran or Malayan plantation oils are the highest grade oils, they are sold on the basis of a 5% content of free fatty acids, calculated as oleic acid They may contain as little as 3% of free acids Congo plantation oils are sold on the basis of their containing 10% of free acids African palm oils obtained from wild trees are classified as "soft," "semisoft," or "hard " Soft oils are quoted on the basis of a 12% free fatty acid content, semisoft or mixed oils are quoted on the basis of 35% free acids, and hard oils on the basis of 45% or more

Palm oil is colored a deep orange red by the large amount of carotene which it contains (0 05–0 20%) The color is not much affected by re fining, but palm oil is bleached to a yellow color similar to that of other vegetable oils by hydrogenation It is also bleached by high temperature treatment with fuller's earth, by deodorization or other high temperature treatment, or by oxidation, either by air or chemical means It has a pleasant, characteristic odor, is very stable toward oxidation, and has no drying

[57] See *Oil & Soap*, **13**, 264 (1936)

properties At ordinary temperatures of 70° to 80°F it is semisolid Its consistency and melting point depend to a large degree upon its content of free fatty acids, as the free acids are higher in melting point than the glycerides To the palm oil trade, oils with a relatively low free acid content are known as soft oils, whereas those with a high acidity are termed hard oils

Average characteristics of palm oil from the Netherlands East Indies and Malaya are approximately as follows iodine value, 53, saponification value, 198, refractive index at 60°C, 1 4510, density at 60°C, 0 884, unsaponifiable matter, 0 4%, titer, 43 5°C Some of the African palm oil from uncultivated trees may be as high as 60 in iodine value, iodine values below 50 have occasionally been reported

TABLE 81
COMPOSITION IN PER CENT BY WEIGHT OF PALM OILS

Analysis	Cape Palmas (native)[a]	Grand Bassa (native)[a]	Belgian Congo (native)[a]	Cameroons (native)[a]	Malaya (plantation)[b]
Iodine value	60 0	55 6	54 1	53 3	53 8
Saponification equivalent	283 8	282 6	280 1	282 5	282 3
Fatty acids					
Myristic	1 6	0 6	1 3	1 1	1 4
Palmitic	32 3	37 6	41 4	45 1	40 1
Stearic	5 5	3 7	4 7	4 1	5 5
Hexadecenoic	—	1 4	—	0 8	—
Oleic	52 4	50 3	42 9	38 6	42 7
Linoleic	8 2	6 4	9 7	10 3	10 3
Glycerides (probable composition)					
Tripalmitin	2	3	5 5	5	—
Dipalmitostearin	1 5	3	1	3 5	—
Oleodipalmitin	16 5	31	29 5	43	—
Oleopalmitostearin	16	10	13 5	11	—
Palmitodiolein	51	41	44 5	31	—
Triolein	14	12	6	6 5	—

[a] T P Hilditch and L Maddison *J Soc Chem Ind* 59, 67–71 (1940)
[b] T P Hilditch and E E Jones, *ibid*, 49, 363 368T (1930), 50, 171–176T (1931)

Following are the A O C S recommended standards for palm oil [57a]

Specific gravity at 100°F (37 8°C)	0 898–0 901
Refractive index at 40°C	1 453–1 456
Iodine value	44–58
Saponification value	195–205
Unsaponifiable matter, %	Not over 0 8
Titer, °C	40–47

[57a] See *Oil & Soap*, 20, 163–164 (1943)

Because of the investigations of Hilditch and co workers [53] the composition of palm oils from different sources is very accurately known A number of analyses are recorded in Table 81

There are no distinctive color tests for palm oil, hence this oil is somewhat difficult to detect in admixture with hydrogenated fats However, palm oil or hydrogenated palm oil generally develops a slight, distinctive violet like odor after limited oxidation, hence the presence of this oil is often indi cated qualitatively by the appearance of such an odor during the course of stability or accelerated oxidation tests

(e) *Sunflowerseed Oil*

In the crude form, sunflowerseed oil is light amber in color, the color of the refined oil is a pale yellow, similar to that of many other vegetable seed oils The crude oil contains some phosphatides and mucilaginous matter, but less than cottonseed or corn oil Its free fatty acid content is similar to

TABLE 82
CHARACTERISTICS AND COMPOSITION IN PER CENT BY WEIGHT OF SUNFLOWERSEED OIL

Analysis	Jamieson and Baughman[a]	Hilditch and Zaky[b]
Iodine value	130 8	138 2
Saponification value	188 0	190
Specific gravity at 25°/25°C	0 9193	—
Refractive index at 20°C	1 4736	—
Unsaponifiable matter, %	1 20	—
Fatty acids		
Palmitic	3 6	5 6
Stearic	2 9	2 2
Arachidic	0 6	0 9
Lignoceric	0 4	—
Oleic	34 0	25 1
Linoleic	57 5	66 2

[a] G S Jamieson and W F Baughman *J Am Chem Soc* 44 2952 2957 (1922)
[b] T P Hilditch and Y A H Zaky, *Biochem J*, 36, 815–821 (1942)

that of most other seed oils, *i e*, 0 5% and above Sunflowerseed oil has a distinctive, not unpleasant odor which is completely removed by steam deodorization

Average characteristics of refined sunflower oil are approximately as follows iodine value, 130, refractive index at 60°C, 1 4599, saponification value, 190, density at 60°C, 0 897, titer, 18°C, unsaponifiable matter, 0 8%

[53] T P H ... 368T (1930, 50, 171–176T ... T (1933) A Banks, H K ... P Hilditch and L Maddison, *ibid*, 59, 67–71 (1940)

The A O C S recommended standard for sunflowerseed oil is as follows [57a]

Specific gravity at 25°/25°C	0 915-0 919
Refractive index at 25°C	1 472-1 474
Iodine value	125-136
Saponification value	188-194
Unsaponifiable matter, %	Not over 1 5
Titer °C	16-20

The composition of sunflowerseed oil, as reported by two different groups of analysts, is shown in Table 82 Of these two oils, the sample examined by Jamieson and Baughman was from seed grown in the United States The source of the sample examined by Hilditch and Zaky was not stated Russian sunflowerseed oils analyzed by different workers[59] have generally been intermediate in composition between the two samples of Table 82

There are no tests for the detection of sunflowerseed oil in other oils

(f) Sesame Oil

Crude sesame oil varies from amber to yellow in color It refines to a pale yellow Sesame oil is relatively high in unsaponifiable substances, but these consist largely of sterols and other substances which are not removable by refining It is relatively low in other nonoil materials

The unsaponifiable fraction of sesame oil contains a class of substances, sesamin, sesamoline, etc [60] which give distinctive color reactions (the well known Baudouin and Villavecchia tests[49]), hence sesame oil is readily detected even in small amounts in other oils, even after hydrogenation The unusual stability of sesame oil is possibly attributable to the antioxidant effect of some of the same substances

The free fatty acid content of crude sesame oil expressed from undamaged seed is the same as that of other common seed oils, *i e*, about 0 5-1 0%

The sesame oils examined by the author have all had iodine values within the range of 109 to 113, although values as low as 103 and as high as 116 have been reported in the literature Sesame oil does not cloud at temperatures down to 0°C Average values for other characteristics are approximately as follows saponification value, 191, refractive index, at 60°C, 1 4582, density at 60°C, 0 892, titer, 23°C, unsaponifiable matter, 1 0%

The A O C S recommended standard for sesame oil is as follows [51]

Specific gravity at 25°/25°C	0 914-0 919
Refractive index at 25°C	1 470-1 474
Iodine value	103-116

[59] See T P Hilditch *The Chemical Constitution of Natural Fats* Wiley, New York, 1941, p 128

[60] See Y Villavecchia and G Fabris *J Soc Chem Ind* 13, 69 (1894) W Adriani, *Z Untersuch Lebensm* 56, 187 (1928) J Böeseken, W Cohen and C Kip, *Rec trav chim*, 55, 816 (1936)

Saponification value	188–195
Unsaponifiable matter, %	Not over 1 8
Titer, °C	20–24

The analyses of sesame oil reported by two different groups of workers are reported in Table 83

(g) Corn Oil

Crude corn or maize oil has a dark reddish amber color, and after refining is considerably darker in color than most other vegetable oils It contains relatively large amounts of phosphatides and other nonoil substances

TABLE 83

CHARACTERISTICS AND COMPOSITION IN PER CENT BY WEIGHT OF SESAME OIL

Analysis	India[a]	China[b]
Iodine value	109 6	110 8
Saponification value	190	189 3
Specific gravity at 25°/25°C	—	0 9187
Refractive index at 20°C	—	1 4731
Fatty acids		
Palmitic	9 1	7 8
Stearic	4 3	4 7
Arachidic	0 8	0 4
Oleic	45 4	49 4
Linoleic	40 4	37 7

[a] T P Hilditch M B Ichaporia, and H Jasperson, *J Soc Chem Ind*, **57**, 363–368T (1938)

[b] G S Jamieson and W F Baughman, *J Am Chem Soc*, **41**, 775–778 (1928)

(often 2% or more) and its free fatty acid content (usually above 1 5%) is higher than that of other common vegetable seed oils of good quality The refined oil contains traces of wax, which cause the oil to cloud when cooled to a low temperature unless they are removed by winterization It has a characteristic sweetish odor reminiscent of corn sugar, which is completely removed by deodorization

Jamieson and Baughman[61] found a number of samples of refined corn oil to have the following average characteristics iodine value, 126 0, saponification value, 190 6, specific gravity, 25°/25°C, 0 9198, refractive index at 20°C, 1 4748, unsaponifiable matter, 1 25%, saturated fatty acids, 9 4%, unsaturated fatty acids, 85 6% These values appear to be very near the average for American oils The titer of corn oil averages about 18°C

[61] G S Jamieson and W F Baughman, *Cotton Oil Press*, **7**, No 12, 34 (1924)

The A O C S standard for corn oil is as follows.[51]

Specific gravity at 25°/25°C	0 915–0 920
Refractive index at 25°C	1 470–1 474
Iodine value	103–128
Saponification value	187–193
Unsaponifiable matter, %	Not over 2 0
Titer, °C	14–20

Compositions reported for two different samples of corn oil are shown in Table 84

There are no tests for the detection of corn oil in other oils

TABLE 84
CHARACTERISTICS AND COMPOSITION IN PER CENT BY WEIGHT OF CORN OIL

Analysis	Jamieson and Baughman[a]	Longenecker[b]
Iodine value	117 2	—
Saponification value	187 3	—
Refractive index at 20°C	1 4717	—
Specific gravity at 25°/25°C	0 9185	—
Unsaponifiable matter, %	1 7	—
Fatty acids		
Myristic	—	1 7
Palmitic	7 8	11 0
Stearic	3 6	2 9
Arachidic	0 4	—
Lignoceric	0 2	—
Hexadecenoic	—	1 6
Oleic	46 3	48 8
Linoleic	41 7	34 0

[a] G S Jamieson and W F Baughman *J Am Chem Soc* **43**, 2696–2702 (1921)
[b] H E Longenecker, *J Biol Chem*, **129**, 13–22 (1939) Figures in mole per cent

(h) *Poppyseed Oil*

Poppyseed oil has an iodine value (about 130 to 140) in the range of the linolenic acid oils, but appears to contain no appreciable amount of linolenic acid, since it yields no ether insoluble bromides

The characteristics and composition of a sample of poppyseed oil examined by Eibner and Wibelitz[62] were as follows saturated acids, 7 2%, oleic acid, 28 3%, linoleic acid, 58 5%, iodine value, 133 4, saponification value, 197 5 Other characteristics of poppyseed oil are approximately as follows density at 60°C, 0 898, refractive index at 60°C, 1 4604, unsaponifiable matter, 0 5%, titer, 17°C

There is no method of detecting poppyseed oil in admixture with other oils.

[62] A Eibner and B Wibelitz, *Chem Umschau*, **31**, 109–120, 121–127 (1924)

(i) Teaseed Oil

Teaseed oil, which has the appearance in the crude and refined forms of ordinary vegetable seed oils, is remarkable for being the sole oil of present commercial importance with a composition virtually identical with that of olive oil However, it can be detected in olive oil or other oils in the amount of as little as 5% to 10% by means of the Fitelson test [63]

The average iodine value of teaseed oil appears to be very close to that of olive oil, i e, about 85 Other average characteristics are approximately as follows saponification value, 192, refractive index at 60°C, 1 4545, density at 60°C, 0 887, titer, 22°C

A sample of teaseed oil with an iodine value of 86 3 examined by Griffiths, Hilditch, and Jones[64] contained the following fatty acids (in per cent) myristic, 0 3, palmitic, 7 6, stearic, 0 8, arachidic, 0 6, oleic, 83 3, and linoleic, 7 4

(j) Kapok Oil

Kapok oil is botanically related to cottonseed oil, and gives the Halphen color reaction even more strongly than does cottonseed oil However, it can be distinguished from cottonseed oil by the test proposed by Besson [65] In appearance kapok oil is somewhat lighter than cottonseed oil, and it has a somewhat greenish cast It contains less non oil materials than cotton seed oil

The iodine value of kapok oil appears to vary from about 94 to 100 Reported values for other characteristics are as follows[66,68], saponification value, 191, refractive index at 25°C, 1 4696, unsaponifiable matter, 0 8% to 0 9%, titer, 30 4°C

The composition of a sample of kapok oil with an iodine value of 96 0 was found by Jamieson and McKinney[67] to be as follows in terms of glycerides (including unsaponifiable matter) palmitic, 10 2%, stearic, 8 4%, arachidic, 1 2, lignoceric, 0 04, oleic, 45 2, linoleic, 32 9%, and unsaponifiable, 0 8

(k) Rice Bran Oil

All samples of rice bran oil examined by the author as well as those reported by others have been very high in free fatty acids While the free acidity of crude vegetable oils depends in general upon the care exercised in handling the oil bearing material prior to extracting the oil, a rather

[63] J Fitelson J Assoc Official Agr Chem, 19, 493–497 (1936)

[64] H N Griffiths T P Hilditch, and E C Jones, J Soc Chem Ind, 53, 13 21T (1934)

[65] A A Besson, Chem Ztg 38, 982 (1914) J Soc Chem Ind 34, 184 (1915)

[66] [illegible] 909 (1931)

[67] [illegible] 34 (1936)

[68] [illegible]

high acidity is probably more or less inherent in this oil, since the rice bran contains an unusually active lipase [69]

Good grades of rice bran oil may be quite light in color, although somewhat greenish, particularly after hydrogenation Rice bran oil appears to contain unusually potent antioxidants, which render the oil very resistant to oxidation, both before and after hydrogenation

The following analysis was reported by Jamieson[70] of a sample of oil derived from American rice

Iodine value	99 9
Saponification value	185 3
Acid value	73 7
Unsaponifiable matter	4 64%
Myristic acid	0 5%
Palmitic acid	11 7%
Stearic acid	1 7%
Arachidic acid	0 5%
Lignoceric acid	0 4%
Oleic acid	39 2%
Linoleic acid	35 1%

(l) Other Oleic Linoleic Acid Oils

Almond oil has been examined with respect to its fatty acid and glyceride compositions by Gunde and Hilditch,[71] who reported the following myristic acid, 1 2%, palmitic acid, 4 5%, oleic acid, 77 0%, linoleic acid, 17 3%, monosaturated dioleins, 17%, linoleodioleins, 52%, triolein, 31% Bush and Lasher[72] found the iodine values of oils from five varieties of almonds to vary from 102 0 to 105 7

The following composition was reported by Bickford, Mann, and Markley[73] for a sample of *pecan* oil with an iodine value of 104 5 saturated acids, 4 0%, oleic acid, 70 9, linoleic acid, 25 2, unsaponifiable matter, 0 4%

The following analysis of *apricot* kernel oil was reported by Jamieson and McKinney [74] iodine value, 108 7, saponification value, 190 2, saturated acids, 3 6%, oleic acid, 60 6%, linoleic acid, 30 0% *Peach kernel* and *plum kernel* oils are very similar to apricot kernel oil

Jamieson, Baughman, and Gertler[75] reported the following analysis of *grapefruit seed* oil iodine value, 106 3, saponification value, 194 1, unsaponifiable matter, 0 7%, palmitic acid, 19 2%, stearic acid, 7 3%, lignoceric acid, 0 2%, oleic acid, 19 7%, linoleic acid, 48 8%

[69] C A Browne *J Am Chem Soc* 25, 948–954 (1903)
[70] G S Jamieson *Oil & Fat Industries* 3, 256–261 (1926)
[71] *Chem Ind* 59 47–53 (1940)
[72]
[73] 20, 85–89 (1943)
[74] 33)
[75] G S Jamieson W F Baugh *Ind* , 7, 181–183 (1930)

6 The Erucic Acid Oils

(a) *Rapeseed Oil*

Rapeseed oil, which is dark yellow or amber in the crude form, refines to a yellow color similar to that of other seed oils The crude oil contains considerable quantities of phosphatides and other impurities The refined oil has a characteristic pungent, mustard like odor, which is removed by deodorization However, deodorized rapeseed oil is somewhat inclined to revert in flavor and acquire an unpleasant taste different from that of the

TABLE 85

COMPOSITION IN PER CENT BY WEIGHT OF RAPESEED AND OTHER ERUCIC ACID OILS

Analysis	Rapeseed (Indian)[a]	Rapeseed (English)[b]	Mustard black seed (Indian)[c]	Mustard black seed (English)[b]	Mustard white seed (English)[b]	Ravison (Danubian)[b]
Iodine value	—	102 9	—	104 0	95 4	112 6
Saponification equivalent	—	318 8	—	326 0	310 0	313 4
Saponification value	172	176	180	172	181	179
Unsaponifiable matter, %	—	1 1	—	3 3	4 6	2 2
Fatty acids						
Myristic	1 5	—	0 5	—	—	—
Palmitic	—	1	—	2	2	2
Stearic	1 6	—	—	Trace	Trace	—
Arachidic	—	—	—	Trace	1	—
Behenic	0 5	—	3 8	—	—	Trace
Lignoceric	2 4	1	1 1	2	1	2
Oleic	20 2	32	32 3	24 5	28	20 5
Erucic	57 2	50	41 5	50	52 5	47 5
Linoleic	14 5	15	18 1	19 5	14 5	25 5
Linolenic	2 1	1	2 7	2	1	2

[a] J J Sudborough H E Watson P R Ayyar, and N R Damle, *J Indian Inst Sci* 9A, 25 (1926)

[b] T P Hilditch T Riley and N L Vidyarthi, *J Soc Chem Ind*, 46, 457–467T (1927)

[c] J J Sudborough H E Watson P R Ayyar, and V M Mascarenhas, *J Indian Inst Sci*, 9A, 43 51 (1926)

undeodorized oil Refined or otherwise processed rapeseed oil is often called colza oil

The A O C S standard for rapeseed oil is as follows [51]

Specific gravity at 25°/25°C	0 906-0 910
Refractive index at 25°C	1 470-1 474
Iodine value	97–108
Saponification value	170–180
Unsaponifiable matter, %	Not over 1 5
Titer, °C	11 5–15 0
Viscosity (Saybolt Universal at 100°C), seconds	Not less than 210
Flash point, open cup, °F	Not less than 550
Ether insoluble bromides, %	Not over 4%
Cold test (A S T M) °F	Not over 10

Rapeseed oil (and the other erucic acid oils) is distinguished by its low saponification value, high refractive index in relation to the iodine value, low titer, and low solidification or clouding temperature It is also slightly more viscous than ordinary oils

The composition of rapeseed oil, as reported by different analysts is shown in Table 85

(b) *Other Erucic Acid Oils*

Mustard seed and *ravison* oils are obtained from the seeds of plants closely related to rape, and are very similar to rapeseed oil in composition The characteristics and compositions of these oils are indicated in Table 85

7. The Linolenic Acid Oils

Only recently have methods become available for accurately estimating the fatty acid composition of oils containing linolenic acid With respect to their analysis, the linolenic acid oils present a much more difficult problem than the oleic linoleic acid oils It has long been known that a reasonably good separation of unsaturated and saturated C_{16} and C_{18} acids can be made on the basis of relative insolubility of the lead soaps of the latter in cold ether or alcohol Hence, for oils containing only oleic and linoleic acids as unsaturated acids it has been an easy matter to calculate the proportions of saturated, oleic, and linoleic acids from the yield and iodine value of the unsaturated fraction No such calculation is of course possible when linolenic acid is likewise present While better methods are now available for the analysis of oleic linoleic acid oils, the lead soap technique may be considered still sound, and reasonably accurate The same, however, cannot be said of older methods for the analysis of linolenic acid oils

Prior to about 1926 it was customary to estimate linoleic and linolenic acids from the yields of petroleum ether and ether insoluble tetrabromides and hexabromides resulting from bromination of the mixed fatty acids It is now known that this procedure produces yields of the bromides which are both low and unpredictable, hence analyses based upon it are seriously in error

Since the introduction by Kaufmann[76] in 1926 of the thiocyanogenometric method, calculations of the composition of linolenic acid oils have generally been made upon the basis of iodine and thiocyanogen values It was assumed by Kaufmann that thiocyanogen was added quantitatively at one double bond in oleic acid, one double bond in linoleic acid, and two double bonds in linolenic acid Hence, after the saturated acids have been determined by some other method, determinations of the iodine and thio

[76] H P Kaufmann *Z Untersuch Lebensm* , 51, 15-27 (1926), *Ber* , 70B, 2545-2549 (1937)

cyanogen values provide data for the calculation of the composition of the oil in terms of its oleic, linoleic, and linolenic acids. Most of the analyses reported between about 1926 and 1940 were calculated upon this basis.

Although discrepancy between the actual and theoretical absorption of thiocyanogen was first pointed out by Kimura[77] in 1929, the shortcomings of Kaufmann's original methods of calculation were not generally recognized, and the basis for accurate calculations was not established until after the much later work of Kass, Wheeler, Hilditch, Riemenschneider, and Matthews, and their co workers, published during the period 1939 to 1941.[78] It has been shown by these workers that the addition of thiocyanogen to the acids mentioned above not only differs somewhat from that originally assumed, but also varies according to the strength of the reagent, the reaction time, and the excess of reagent employed. However, by standardizing these variables *it is possible to employ empirical thiocyanogen values for* the various acids which accurately express the composition of oils or fatty acid mixtures.[78]

The magnitude of the errors introduced by using the theoretical rather than the empirical thiocyanogen values is illustrated by the following example, taken from the work of Rose and Jamieson[79] on a sample of linseed oil.

Acids	Composition, calculated from theoretical thiocyanogen values %	Composition calculated from empirical thiocyanogen values %
Saturated acids	9.5	9.5
Oleic acid	9.9	19.0
Linoleic acid	42.1	24.1
Linolenic acid	38.5	47.4

Use of the incorrect theoretical thiocyanogen values, it will be observed, has the effect of making the calculated amounts of oleic and linolenic acid much too low, and the amount of linoleic acid correspondingly high.

Although in the case of some of the linolenic acid oils, notably linseed oil, recent analyses have been reported in which correct thiocyanogen values were used, there are still a number of these oils whose compositions as last reported are undoubtedly much in error from the use of the incorrect

[77] W. Kimura, *J. Soc. Chem. Ind. Japan*, **32**, 138–141B (1929).

[78] See R. W. Riemenschneider and D. H. Wheeler, *Oil & Soap*, **16**, 219–221 (1939); R. W. Riemenschneider, C. E. Swift, and C. E. Sando, *ibid.*, **18**, 203–206 (1941); D. H. Wheeler, R. W. Riemenschneider, and C. E. Sando, *J. Biol. Chem.*, **132**, 687–699 (1940); J. P. Kass, H. G. Loeb, F. A. Norris, and G. O. Burr, *Oil & Soap*, **17**, 118–119 (1940); J. P. Kass, W. O. Lundberg, and G. O. Burr, *ibid.*, **17**, 50–53 (1940); T. P. Hilditch and K. S. Murti, *Analyst*, **65**, 437–446 (1940); N. L. Matthews, W. P. Brode, and J. B. Brown, *Oil & Soap*, **18**, 182–187 (1941).

[79] W. G. Rose and G. S. Jamieson, *Oil & Soap*, **18**, 173–174 (1941).

theoretical values Unfortunately, the analysts have in many cases used odd or unrecorded reaction times, or excesses or strengths of the reagent, and thus have made it impossible for their results to be directly recalculated to a correct basis

Recently Mitchell, Kraybill, and Zscheile[80] have described a new optical method for the quantitative determination of linoleic and linolenic acids, which depends upon alkali isomerization of these acids to form conjugated acids, and estimation of the latter through their spectral absorption in the ultraviolet This method should prove highly useful, particularly for the estimation of amounts of linolenic acid too small to be certainly detected by means of iodine and thiocyanogen values or hexabromide determinations

(a) *Linseed Oil*

Crude linseed oil has a dark amber color, and a strong, characteristic odor The odor of linseed oil (and other linolenic acid oils) appears to be associated to some extent with the highly unsaturated acids of the oil, it is inclined to recur after the oil has been steam deodorized, hence unlike that of the oleic linoleic acid oils, is not derived solely from volatile impurities in the oil The color of linseed oil can be reduced to a pale yellow, similar to that of other refined vegetable oils, by suitable refining and bleaching treatment The free fatty acid content of linseed oil is not different from that of other seed oils of annual plants, *i e*, it ranges upward from about 0 5%, according to the treatment accorded the seed after the latter have reached maturity

The crude oil contains relatively large amounts of phosphatides and mucilaginous materials, which must be separated from the oil before it is utilized in paints or varnishes As in the case of cottonseed or soybean oils, these materials become insoluble upon hydration They are completely removed by alkali refining When the oil is heated rapidly to a high temperature, these materials separate in the form of "break material," which in the case of crude oils amounts to about 0 1–0 5% of the weight of the oil Refined oils should contain no break material Refined linseed oil contains traces of waxes, which separate when the oil is chilled to a low temperature, and are removed from "wintered" oil

The quality of linseed oil for technical purposes (or for use as a drying oil) is dependent largely upon its degree of unsaturation, as indicated by its iodine value Since this property is quite variable, it is necessary to blend lots of oil from different sources, in order to obtain commercial oils of consistently high iodine value Although the average Wijs iodine value of linseed oil from Canada, the United States, or Argentina is probably between 180 and 185, occasional lots are produced, under unusual climatic

[80] J H Mitchell, H R Kraybill and F P Zscheile *Ind Eng Chem Anal Ed* 15, 1 3 (1943)

conditions, with iodine values above 200, or as low as 130 to 140.[81] With *other factors equal, the colder the climate in which flaxseed is grown, the* higher is the iodine value of the oil. There are also important differences in the oil from different varieties of flaxseed grown under the same conditions.[81, 82] The requirements of A.S.T.M. specification D234–28 for linseed oil (raw) are as follows:

Specific gravity at 15.5°/15.5°C	0.931–0.936
Acid number, maximum	4.0
Saponification value	189–195
Unsaponifiable matter, %, maximum	1.50
Iodine value (Wijs), minimum	177

The refractive index of linseed oil varies with the iodine value; an average value for an oil with an iodine value of 180 is about 1.468 at 60°C. The titer of linseed oil is about 18°C.

The composition of samples of linseed oil of different iodine values, according to recent analyses which may be considered trustworthy, are recorded in Table 86.

TABLE 86

COMPOSITION IN PER CENT BY WEIGHT OF NORTH AMERICAN LINSEED OILS OF DIFFERENT IODINE VALUES

Analysis	Painter and Nesbitt[a]	Painter and Nesbitt[a]	Painter and Nesbitt[a]	Rose and Jamieson[b]	Painter and Nesbitt[a]	Painter and Nesbitt[a]
Iodine value	127.8	164.8	176.8	179.8	193.6	202.8
Refractive index at 25°C	—	—	—	1.4784	—	—
Unsaponifiable matter, %	1.34	0.94	0.85	1.11	0.79	0.91
Fatty acids						
Palmitic	—	—	—	6.3	—	—
Stearic	—	—	—	2.5	—	—
Arachidic	—	—	—	0.5	—	—
Lignoceric	—	—	—	0.2	—	—
Total saturated	16.3	11.8	8.9	9.5	10.3	7.3
Oleic	40.5	26.4	25.3	19.0	15.6	14.2
Linoleic	22.7	22.2	19.2	24.1	15.4	16.7
Linolenic	20.5	39.6	46.5	47.4	58.7	61.8

[a] E. P. Painter and L. L. Nesbitt, *Ind. Eng. Chem., Anal. Ed.* **15**, 123–128 (1943).
[b] W. G. Rose and G. S. Jamieson, *Oil & Soap*, **18**, 173–176 (1941).

(b) *Soybean Oil*

Crude soybean oil[83] of good quality has a light amber color, which upon alkali refining is reduced to the light yellow of most vegetable seed oils.

[81] E. P. Painter and L. L. Nesbitt, *Ind. Eng. Chem., Anal. Ed.*, **15**, 123–128 (1943).
[82] A. C. Dillman and T. H. Hopper, *U. S. Dept. Agr. Tech. Bull.* No. 844 (1943). E. P. Painter and L. L. Nesbitt, *Oil & Soap*, **20**, 208–211 (1943).
[83] The composition and characteristics of soybean oil are discussed in detail in the monograph by K. S. Markley and W. H. Goss, *Soybean Chemistry and Technology*, Chem. Pub. Co., New York, 1944.

Soybean oil produced from green or immature beans may contain sufficient chlorophyll to have a greenish cast, which, however, is not usually very evident until after the yellow red pigments of the oil have been reduced by hydrogenation Oil produced from badly damaged beans may have a dark brown color difficult or impossible to fully remove by refining and bleaching

The crude oil, and particularly that obtained by solvent extraction contains relatively large amounts (1 5% to 2 5%) of nonglyceride materials consisting chiefly of phosphatides However, before it is marketed the crude oil is usually greatly reduced in phosphatide content by water washing The free fatty acid content of good crude soybean oil, like that of many other vegetable oils, is slightly in excess of 0 5%

TABLE 87
COMPOSITION IN PER CENT BY WEIGHT OF SOYBEAN OILS OF DIFFERENT IODINE VALUES

Analysis	Dunfield[a]	Dunfield[a]	Unstated variety[b]	Illini[a]	Seneca[a]	Wild beans[a]
Iodine value	102 9	124 0	130 4	131 6	139 4	151 4
Acids below myristic	—	—	0 2	—	—	—
Myristic acid	—	—	0 1	—	—	—
Palmitic acid	—	—	9 8	—	—	—
Stearic acid	—	—	2 4	—	—	—
Arachidic acid	—	—	0 9	—	—	—
Total saturated acids	12 0	13 2	13 4	12 7	11 9	13 5
Tetradecenoic acid	—	—	0 1	—	—	—
Hexadecenoic (including hexadecadienoic) acid	—	—	0 4	—	—	—
Oleic acid	60 0	34 0	28 9	27 7	24 7	11 5
Linoleic acid	25 0	49 1	50 7	53 7	55 4	63 1
Linolenic acid	2 9	3 6	6 5	5 9	8 0	12 1

[a] F G Dollear P Krauczunas and K S Markley, *Oil & Soap* 17, 120–121 (1940)
[b] T P Hilditch and H Jasperson, *J Soc Chem Ind*, 58 187 189 (1939)

Soybean oil has a typical "beany" odor and flavor Like that of other linolenic acid oils, the odor and flavor of soybean oil is inclined to return after the oil has been rendered completely odorless and flavorless by high temperature steam deodorization

The average iodine value of the soybean oil produced in the United States is in the neighborhood of 130, although iodine values as high as 140 and as low as 103 have been reported Other average characteristics are approximately as follows saponification value, 192, refractive index at 60°C, 1 4600, density at 60°C, 0 898, unsaponifiable matter, 0 6%, titer, 24°C

The A O C S recommended standard for soybean oil is as follows[84]

Specific gravity at 25°/25°C	0 917–0 921
Iodine value (Wijs)	120–141

[84] See *Oil & Soap*, 17, 151 (1940).

Saponification value	189–195
Unsaponifiable matter, %	Not over 1 5
Refractive index at 25°C	1 470–1 476

Recent analyses of soybean oil in terms of its component fatty acids are shown in Table 87 In this table are included the analysis reported by Dollear, Krauczunas, and Markley[85] of a soybean oil with the abnormally low iodine value of 102 9 It will be noted that even at this low iodine value soybean oil still contains an appreciable quantity of linolenic acid It was noted in another publication by the same authors[86] that the ratio between saturated and unsaturated fatty acids in soybean oils is fairly constant, variations in iodine value being occasioned by differences in the relative proportions of the different unsaturated acids Scholfield and Bull[87] have presented equations for the estimation of the approximate fatty acid composition of soybean oil from the iodine value These are as follows

$$\text{Per cent saturated acids} = 20\ 5 - 0\ 045\ \text{I V}$$
$$\text{Per cent oleic acid} = 128\ 3 - 0\ 792\ \text{I V}$$
$$\text{Per cent linoleic acid} = -31\ 9 + 0\ 669\ \text{I V}$$
$$\text{Per cent linolenic acid} = -17\ 0 + 0\ 170\ \text{I V}$$

(c) *Perilla Oil*

Crude perilla oil somewhat resembles linseed oil in odor and appearance However, it is said to yield no break material upon being heated to a high temperature, hence it may be presumed that its content of phosphatides or other nonoil substances is very low The free fatty acid content of good perilla oil does not appear to be different from that of linseed oil

The average iodine value of perilla oil is about 195 Reported analyses of this oil indicate that its iodine value may vary less widely than that of linseed oil, thus, for example Jamieson[87a] lists a range of iodine values of 185 to 208 Other average characteristics are approximately as follows saponification value, 192, refractive index at 25°C, 1 481, unsaponifiable matter, 1 0%, density at 15°C, 0 935 The A S T M specification for raw or refined perilla oil is as follows

Specific gravity at 15 5°/15 5°C	0 932
Saponification value, minimum	190
Iodine value (Hanus), minimum	191
Unsaponifiable matter, % maximum	1 5
Acid value, maximum	5 0
Loss on heating at 105°C, %, maximum	0 2

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[85] F [illegible] –264 (1938)
[86] F [illegible] –121 (1940)
[87] C [illegible]
[87a] G S Jamieson, *Vegetable Fats and Oils* 2nd ed, Reinhold, New York, 1943

Wholly acceptable analyses of perilla oil in terms of its component fatty acids do not appear in the literature. The following compositions were reported by Kaufmann[88] in 1930 for two samples of perilla oil: saturated acids 7.2 and 6 3%; oleic acid, 3.7 and 10 1%; linoleic acid, 41.9 and 31 9%, linolenic acid, 41.7 and 46 4%. However, the compositions of these oils were calculated on the basis of theoretical thiocyanogen values for the unsaturated fatty acids, and hence are undoubtedly in error with respect to the relative proportions of the latter.[89]

Riemenschneider, Swift, and Sando[89a] have analyzed a sample of perilla oil with a Wijs iodine value of 203 9, and have calculated its composition with the aid of new, empirical thiocyanogen values for the various unsaturated acids. The composition was as follows: saturated acids, 9 56%; oleic acid, 17.97%; linoleic acid, 0 00%; linolenic acid, 72 47%. It appears unlikely that the oil could actually be quite devoid of linoleic acid; nevertheless the composition reported is undoubtedly more nearly the true one than any estimated by previous workers.

(d) *Safflower Oil*

Safflower oil is somewhat similar in appearance and composition to a high iodine value soybean oil. The average iodine value of this oil appears to be about 145 Other average characteristics are about as follows: saponification value, 192, refractive index at 60°C., 1.462; density at 60°C., 0 900; unsaponifiable matter, 1.0%; titer, 16°C.

Recent and hence presumably trustworthy estimations of the composition of safflower oil have been furnished by Vidyarthi[90] and by Bickford, Mann, and Markley.[73] The data of Vidyarthi on an Indian safflower oil are as follows:

Iodine value of oil	136 2
Lauric acid and lower acids	0.4%
Myristic acid	1.1%
Palmitic acid	2 9%
Stearic acid	1.1%
Arachidic and lignoceric acids	0 5%
Oleic acid	32 8%
Linoleic acid	61.1%
Linolenic acid	0 1%

[88] H. P. Kaufmann, *Allgem Oel- u Fett-Ztg*, 27, 39–40 (1930).

[89] See the discussion of methods of determining the composition of linolenic acid oils (pages 168–170).

[89a] R. W Riemenschneider, C. E. Swift, and C E Sando, *Oil & Soap*, 18, 203-206 (1941)

[90] N. L. Vidyarthi, *J. Indian Chem. Soc.*, 20, 45–50 (1943).

Bickford *et al* found the acids from a sample of American safflower oil with an iodine value of 146 5 to consist of the following saturated acids, 6 8%, oleic acid, 18 6%, linoleic acid, 70 1%, linolenic acid, 3 4%

(e) *Hempseed Oil*

Hempseed oil, which is seldom seen in the United States, is said to be somewhat similar to low iodine value linseed oil in odor, properties, and general appearance, except that it is somewhat greenish in color

The iodine values reported for hempseed oil range from about 150 to 175 Kaufmann and Juschkewitsch[91] and Griffiths and Hilditch[92] found the composition of hempseed oil to be as follows

	Kaufmann and Juschkewitsch	Griffiths and Hilditch
Iodine value	167 0	174 4
Saturated acids, %	10 1	8 6
Oleic acid	12 6	6 7
Linoleic acid	53 0	68 8
Linolenic acid	24 3	15 9

The above analyses, reported in 1930 and 1934, respectively, are undoubtedly in error with respect to the amounts of the different unsaturated acids [89] The true linoleic acid content of hempseed is probably lower than is indicated above and the contents of oleic and linolenic acid correspondingly higher

(f) *Other Linolenic Acid Oils*

Cedar nut oil, which is unknown in the United States, but is apparently of some commercial importance in Russia, is reported to have an iodine value ranging from 150 to 160, and to be otherwise similar in characteristics to other drying oils of equivalent unsaturation In addition to about 8% of saturated acids it is reported to contain the following unsaturated acids [93] oleic acid, 32 5 to 35 8%, linoleic acid, 31 1 to 34 2%, linolenic acid, 16 6 to 27 8%

A sample of crude *chiaseed* oil was examined by Baughman and Jamieson[94] and found to have the following characteristics specific gravity at 25°/25°C, 0 9358, refractive index at 20°C, 1 4838, acid value, 1 4, saponification value, 194 8, unsaponifiable matter, 0 7%, iodine value (Hanus), 190 0 The composition of the fatty acids, as calculated from the iodine and thiocyanogen values was as follows saturated, 8 7%, oleic, 0 8%, linoleic, 48 4, linolenic, 42 1 This calculation, reported in 1929,

[91] [illegible] –91 (1930)
[92] [illegible] (1934)
[93] [illegible] *Forsch Inst Nahr u Genussmittelind U S S R* 3, 239–245 (1933)
[94] W F Baughman and G S Jamieson *Oil & Fat Industries* 6, No 9 15–17 (1929)

may be presumed to be somewhat in error.[89] The true oleic and linolenic acid contents of the oil are undoubtedly higher, and the linoleic acid content lower.

A sample of *candlenut* or *lumbang* oil from the Phillipines was examined by Jamieson and McKinney[95] and found to have the following characteristics and composition: specific gravity at 25°/25°C., 0 9233; refractive index at 25°C , 1.4749; saponification value, 190.8; iodine value (Hanus), 151.7; acid value, 1.15; unsaponifiable matter, 0.30%; palmitic acid, 4.6%; stearic acid, 4 1%; arachidic acid, 0.1%; oleic acid, 27.6%; linoleic acid, 41.8%; linolenic acid, 21.8%. For reasons stated previously,[89] the accuracy of this analysis may be considered questionable. Although the candlenut tree is botanically related to the tung tree, candlenut oil contains no elaeostearic acid.

The analyses of *rubberseed* oil have been recorded by Jamieson and Baughman[96] and Griffiths and Hilditch[92] as follows:

	Jamieson and Baughman	Griffiths and Hilditch
Iodine value	135.2	140.3
Unsaponifiable matter, %	0 8	—
Palmitic acid, %	7.4	—
Stearic acid, %	9.2	—
Arachidic acid, %	0 3	—
Total saturated acids, %	16.9	18.4
Oleic acid, %	28.9	23 6
Linoleic acid, %	33 4	43.3
Linolenic acid, %	20 8	14 7

The above analyses, reported in 1930 and 1934, respectively, cannot be considered accurate with respect to the proportions of the different unsaturated fatty acids.[89]

Analyses of the oils from *English walnuts* and American *black walnuts*, as reported respectively by Griffiths and Hilditch[92] and by Jamieson and McKinney[97] are as follows:

	English walnut	Black walnut
Iodine value	155 7	135 1
Saturated acids	8.1	5.8
Oleic acid	19.1	36 6
Linoleic acid	65.9	50 0
Linolenic acid acid	6.9	7.6

As in the case of many other analyses of drying oils,[89] the above figures are probably inaccurate insofar as the proportions of the unsaturated fatty acids are concerned.

A sample of Chinese *stillingia* oil examined by Jamieson and McKinney[98]

[95] G. S. Jamieson and R. S McKinney, *Oil & Soap*, 14, 203–205 (1937).

[96] [illegible] 419–421, 437 (1930)

[97] [illegible] 6)

[98] [illegible] 938).

had an iodine value of 169 0 and the following fatty acid composition saturated, 9 4%, oleic, 11 1%, linoleic, 52 7%, linolenic 26 8% However, the estimated amounts of the different unsaturated acids are presumably in error[89]

Wheat germ oil is principally of interest because of its high content (circa 0 5%) of tocopherols (vitamin E) The iodine value of this oil appears to average about 125 The unsaponifiable matter in wheat germ oil is high, amounting to about 3–5% Analyses of wheat germ oil in terms of its fatty acids (which analyses have, however, not been made by modern and reliable methods) have been reported respectively by Jamieson and Baughman[99] and Sullivan and Bailey[100] as follows

Iodine value	125 6	125 0
Unsaponifiable matter %	4 7	4 0
Saturated acids %	15 1	16 0
Oleic acid %	30 0	28 1
Linoleic acid %	44 1	52 3
Linolenic acid %	10 8	3 6

8 The Conjugated Acid Oils

What has been said previously with respect to the analysis of linolenic acid oils may be repeated here regarding the conjugated acid oils Due to the limitations of analytical methods available in the past, the older analyses reported in the literature must generally be regarded with some suspicion Recent developments which have contributed toward more trustworthy results in the analysis of these oils include the establishment of accurate empirical thiocyanogen values for oleic and linoleic acids, the establishment of similar empirical values for the diene values of elaeostearic and licanic acids,[101 103] and the perfection of analytical techniques based on the ultraviolet absorption spectra of conjugated fatty acids

A word of explanation is in order regarding the iodine value of conjugated acid oils Whereas in the case of the oils discussed previously the iodine value is generally the characteristic of paramount importance, it is of only minor significance in oils containing conjugated fatty acids The reason for this is twofold In the first place, conjugated acids do not absorb halogens quantitatively, the iodine value of these oils has no absolute theoretical significance It varies according to the conditions under which the test is made, and is always less than that of nonconjugated oils with the same number of double bonds In the second place, the drying properties of these oils are of first importance, and even if it were possible to cause the oils to absorb the theoretical quantity of iodine, or a specific fraction

[99] G S Jamieson and W F Baughman *Oil & Soap*, **9**, 136–138 (1932)
[100] B Sullivan and C H Bailey *J Am Chem Soc* **58**, 383–390 (1936)
[101] R S McKinney and G S Jamieson, *Oil & Soap*, **15**, 30–32 (1938)
[102] R S McKinney N J Halbrook and W G Rose *Oil & Soap*, **19**, 141–143 (1942)
[103] W G Rose and G S Jamieson, *Oil & Soap*, **20**, 227–231 (1943)

thereof, the iodine value would not necessarily measure these properties accurately, since the latter are much more dependent upon the amount of conjugation in the oil than upon the unsaturation of the oil as such

The quality of a conjugated acid oil is *primarily determined by the actual* quantity of conjugated acids which it contains, the latter is indicated more nearly by its gelation time in the Browne or Worstall heat tests[103a] than by any other simple analytical method

(a) Tung Oil

Tung oil (China wood oil) is relatively light in color and relatively free of phosphatides, mucilaginous matter, or other "break material" Since ordinary liquid or "alpha" elaeostearic acid may be rather easily isomerized to a solid "beta" form, tung oil may on occasion contain a precipitate of solid glycerides, or may even completely solidify Isomerization is produced by exposure of the oil to light or to compounds of sulfur, selenium, etc, and also occurs in oil which has been obtained from tung kernels by solvent extraction It may be permanently prevented by heating the oil to 200°C for 30 minutes [104]

A S T M Specification D 12–33 for raw tung oil is as follows

Specific gravity at 15 5°/15 5°C	0 9400–0 9430
Acid number, maximum	8
Saponification value	190–195
Unsaponifiable matter, %, maximum	0 75
Iodine value (Wijs), minimum	163
Refractive index at 25°C	1 5165–1 5200
Heat test (A S T M), minutes, maximum	12

American tung oil of good quality will usually have an acid value well under 1 0, and will gel in the Browne heat test in 9 to 10 minutes Adulterated tung oil will require longer to gel (10% of soybean oil or other nonconjugated acid oil is said to increase the gelation time in the Browne test 2 5 to 3 minutes) and will yield a sticky, rather than a dry, crumbly gel in the A S T M heat test

Diene value determinations are recommended by McKinney, Halbrook, and Rose[102] as a means of detecting adulteration in tung oil Pure tung oil has a maleic anhydride value by the Ellis-Jones method of about 67 to 71, whereas the admixture of 10% of linseed oil with a tung oil lowered the maleic anhydride value from 70 6 to 63 8, and 20% of linseed oil reduced the maleic anhydride value to 56 8 The refractive index of tung oil, it may be observed, is much higher than that of any of the nonconjugated acid oils

[103a] G S Jamieson, *Vegetable Fats and Oils* 2nd ed Reinhold, New York, 1943

[104] W G Rose, A F Freeman, and R S McKinney, *Ind Eng Chem*, 34, 612–614 (1942)

The following is given by McKinney and Jamieson[101] as the fatty acid composition of tung oil saturated acids, 4 6%, oleic acid, 4 1, linoleic acid, 0 6, elaeostearic acid, 90 7

(b) *Oiticica Oil*

Oiticica oil is quite similar to tung oil in most respects However, it dries less strongly, the heat-treated oil on the North American market is said to have a Browne heat test of about 16 minutes, as compared with about 10 minutes for tung oil Untreated oil has a slightly longer gelation time (18–24 minutes)

Oiticica oil undergoes isomerization to a solid form even more readily than does tung oil, and formerly much of the oil reaching the United States was thus solidified The solidified oil may be rendered permanently liquid by heating to above 225°C, and it is the heat-treated oil which is now principally marketed

The following analysis of raw oiticica oil was reported by McKinney and Jamieson [105]

Refractive index at 25°C	1 5145
Saponification value	192 6
Unsaponifiable matter, %	0 57
Saturated acids, %	11 3
Oleic acid	6 2
Licanic acid	82 5

This analysis may be slightly in error, since it was in part calculated from theoretical thiocyanogen values for oleic and licanic acids Morrell and Davis[106] reported the presence of a small amount (*ca* 5%) of elaeostearic acid in oiticica oil

The A O C S recommended standard for oiticica oil is as follows [106a]

Specific gravity at 25°/25°C	0 970–0 978
Refractive index at 25°C	1 500–1 512
Iodine value (Wijs)	140–180
Saponification value	186–193
Unsaponifiable matter, %	Not over 1 0
Titer, °C	42–47
Browne heat test, minutes	Not over 17

(c) *Cacahuanache (Mexican Oiticica) Oil*

Cacahuanache or Mexican oiticica oil appears to be similar to Brazilian oiticica oil in all respects, including the tendency of the latter to isomerize to a solid form after expression Like oiticica oil it may be rendered permanently liquid by being heated to 225°C for a short time

[105] R S McKinney and G S Jamieson, *Oil & Soap* **13**, 10–11 (1936)
[106] R S Morrell and W Davis, *J Oil Colour Chem Assoc*, **19**, 359–362 (1936)
[106a] See *Oil & Soap*, **19**, 140 (1942)

The following characteristics and composition were recently reported for a sample of cacahuanache oil by Rose and Jamieson [103]

Refractive index at 25°C	1 5163
Saponification value	187 3
Iodine value (Wijs one hour)	153 0
Diene value (Ellis Jones)	60 9
Carbonyl value (Leithe)	121 4
Acid value	0 8
Unsaponifiable matter, %	0 5
Browne heat test minutes	15 5
Saturated acids, %	11 6
Oleic acid	5 5
Linoleic acid	7 6
Elaeostearic acid	1 6
Licanic acid	73 7

9 Marine Oils

The marine oils present unusual difficulties to the analyst because of the wide variety of unsaturated fatty acids that they contain Whereas ordinary oils may generally be analyzed in terms of the individual acids, in the case of marine oils it is only possible to estimate the various acids according to their chain lengths, and then determine the average degree of unsaturation existing in the unsaturated acids of each different chain length In the tabulated analyses of these oils in the following section this average degree of unsaturation is expressed in terms of the number of hydrogen atoms lacking to make the acid completely saturated, thus the unsaturation of oleic acid would be expressed as −2 0, that of linoleic acid as −4 0, that of linolenic acid as −6 0, etc In each case the average degree of unsaturation is placed after the percentage of the fatty acid fraction in parentheses, thus, for example, the designation 5 9 (−10 1) means that the oil contains 5 9% of the fatty acids in question, and on the average these acids have a deficiency of 10 1 hydrogen atoms, each (equivalent to just slightly over 5 double bonds each)

(a) *Whale Oil*

According to Brandt,[107] trading in whale oil is conducted under the following grades

Grade	Color	Per cent free fatty acids (as oleic)
1	Pale straw or yellow	Not over 1
2	Amber yellow	1–6
3	Pale brown	6–15
4	Dark	15–60

[107] K Brandt, *Whale Oil An Economic Analysis* Food Research Institute, Stanford University, 1940

In addition to the above, a Grade 0 is also sometimes recognized, consisting of very light colored oil with a free fatty acid content of 0 5% or less Most of the oil now produced may be classified in the higher grades

Whale oil varies a great deal in iodine value, but it would appear that most of the oil derived from whales taken in the Antarctic regions ranges between about 110 and 125 in iodine value Characteristics of whale oil which may be considered somewhat near the average are as follows iodine value, 120, saponification value, 195, refractive index at 60°C, 1 460, density at 60°C, 0 892, unsaponifiable matter, 1 2%, titer, 23°C

The A O C S recommended standard for whale oil is as follows [106a]

Specific gravity at 25°/25°C	0 910–0 920
Refractive index at 25°C	1 470–1 477
Iodine value (Wijs)	110–135
Saponification value	185–202
Unsaponifiable matter, %,	Not over 2 0

The composition of commercial antarctic whale oil, as reported by Hilditch and Terleski[108] and Hilditch and Maddison[109] is as follows

	Hilditch and Terleski	Hilditch and Maddison
Iodine value	100 3	108 0
Saponification equivalent	286 5	287 0
Saturated acids, %		
C_{12}	—	0 2
C_{14}	6 3	9 3
C_{16}	18 2	15 6
C_{18}	2 4	2 8
Unsaturated acids %		
C_{14}	3 7 (−2 0)	2 5 (−2 0)
C_{16}	13 3 (−2 0)	14 4 (−2 1)
C_{18}	38 4 (−2 6)	35 2 (−2 5)
C_{20}	11 4 (−5 6)	13 6 (−7 2)
C_{22}	6 3 (−9 0)	5 9 (−10 1)
C_{24}	—	0 2 (−10 4)

(b) *California Sardine or Pilchard Oil*

Oil derived from the fish *Sardinops caerulea* is known in the United States as sardine oil and in Canada as pilchard oil Japanese sardine oil is obtained from a different species, *Clupanodon melanostica*

Sardine oil, like other fish oils, is somewhat inferior in general quality to whale oil, since it is rendered from the whole fish rather than from selected fatty tissues, and hence contains relatively large amounts of protein decomposition products and other nonfat materials The free fatty acid content of fish oils is also generally somewhat higher than is that of whale oil of good quality

[108] T P Hilditch and J T Terleski, *J Soc Chem Ind*, **56**, 315–322T (1937)
[109] T P Hilditch and L Maddison, *J Soc Chem Ind*, **61**, 169–173 (1942)

From the data of Brocklesby[110] it would appear that sardine oil is consistently higher in iodine value than pilchard oil, average values for the two oils being about 185 and 178, respectively Iodine values below 170 or above 190 are not often observed, in the case of either oil Other average characteristics of sardine oil are approximately as follows saponification value, 191, refractive index at 60°C, 1 4660, density at 60°C, 0 905, unsaponifiable matter, 1 0%, titer, 30°C

The composition of pilchard (sardine) oil has been reported by Brocklesby and Harding[111] to be as follows

	Per cent
Saturated acids	
C_{14}	5 1
C_{16}	14 6
C_{18}	3 2
Unsaturated acids	
C_{14}	Trace
C_{16}	11 8 (−2 0)
C_{18}	17 8 (−3 3)
C_{20}	18 1 (−4 1)
C_{22}	14 0 (−8 5)
C_{24}	15 4 (−10 9)

(c) *Japanese Sardine Oil*

Oil from the Japanese sardine, *Clupanodon melanostica,* appears to differ from American sardine oil in having no appreciable content of C_{24} acids although its iodine value is about the same as that of the American oil Reported iodine values for this oil vary from about 160 to 190

The following composition was given for Japanese sardine oil by Armstrong and Allan [112]

	Per cent
Saturated acids	
C_{14}	5 8
C_{16}	9 7
C_{18}	2 3
Unsaturated acids	
C_{16}	13 0 (−2)
C_{18}	14 2 (−2)
C_{18}	10 0 (−4)
C_{18}	trace (−6)
C_{20}	26 0 (−5)
C_{22}	19 0 (−5)

(d) *Menhaden Oil*

Menhaden oil appears to vary in iodine value and composition somewhat more than sardine oil, iodine values from about 150 to 185 having been

[110] H N Brocklesby, *The Chemistry and Technology of Marine Animal Oils* Fisheries Research Board of Canada, Ottawa, 1941

[111] H N Brocklesby and K F Harding, *J Fisheries Research Board Can*, 4, 59–62 (1938)

[112] E F Armstrong and J Allan, *J Soc Chem Ind*, 43, 207–218T (1924)

reported However, the average iodine value of this oil is probably about 170 Other average characteristics of menhaden oil are approximately as follows saponification value, 191, refractive index at 60°C, 1 4645, density at 60°C, 0 903, unsaponifiable matter, 1 0%, titer, 32°C

The composition of menhaden oil, as reported by Armstrong and Allan[112] is as follows

	Per cent
Saturated acids	
C_{14}	5 9
C_{16}	16 3
C_{18}	0 6
C_{20}	0 6
C_{22}	0 8
Unsaturated acids	
C_{16}	15 5 (−3)
C_{18}	29 6 (−4)
C_{20}	19 0 (−10)
C_{22}	11 7 (−10)

(e) *Herring Oil*

Herring oil varies extremely in composition according to the season, iodine values of 115 to 144 having been observed by Lovern[113] in fish taken from the same waters at different times of the year However, the iodine value of commercial oil may be said to average about 140 Other average characteristics are approximately as follows saponification value, 192, refractive index at 60°C, 1 4610, density at 60°C, 0 900, titer, 25°C

The composition of herring oil with an iodine value of 138 6 was found by Lovern[113] to be as follows

	Per cent
Saturated acids	
C_{14}	7 3
C_{16}	13 0
C_{18}	Trace
Unsaturated acids	
C_{16}	4 9 (−2 7)
C_{18}	20 7 (−4 2)
C_{20}	30 1 (−4 6)
C_{22}	23 2 (−4 3)

(f) *Fish Liver Oils*

Cod liver oil, the most important of the fish liver oils, varies greatly in iodine value, vitamin potency, and general quality The higher grades of cod liver oil are used exclusively as medicinal oils, the term "cod oil" refers to a low grade of liver oil, used principally in leather manufacture Iodine values ranging from about 118 to 186 have been reported for this oil, the average value for commercial oils is probably between 160 and 170 Other average characteristics are as approximately follows saponification value, 186, density at 25°C, 0 925, refractive index at 25°C, 1 481,

[113] J A Lovern *Biochem J*, **32**, 676–680 (1938)

unsaponifiable matter, 1 0%, titer, 18°C The free fatty acid content of medicinal cod liver oil is generally below 0 5%, but that of cod oil may be very high

Cod liver oil contains less saturated acids than other common marine oils but its unsaturated acids do not appear to be different from those of most fish body oils The following analysis, reported by Guha, Hilditch, and Lovern[114] for Newfoundland cod liver oil, is typical·

Iodine value	163 0
Saponification equivalent	301 1
Free fatty acids, %	0 46
Unsaponifiable matter, %	0 87
Saturated acids, %	
C_{14}	5 8
C_{16}	8 4
C_{18}	0 6
Unsaturated acids, %	
C_{14}	0 2
C_{16}	20 0 (−2 3)
C_{18}	29 1 (−2 8)
C_{20}	25 4 (−6 0)
C_{22}	9 6 (−6 9)

In recent years a number of other fish liver oils have attained considerable importance as medicinal oils or sources of vitamin concentrates These include halibut liver oil, tuna liver oil, dogfish liver oil, the liver oil of the soup fin shark and other sharks, etc Most of these oils are much richer sources of vitamin A than is cod liver oil Detailed analyses indicating the compositions of these oils are not generally available

Analyses of cod liver oil and other fish liver oils for vitamin content are given on pages 35–36

10. The Hydroxy Acid Oils

Castor Oil

Castor oil is the only commercially important oil containing major amounts of a hydroxy acid Two grades are recognized by the trade, No 1, which is obtained by the first cold pressing of the beans, is practically colorless, and suitable for medicinal purposes, and No 3, which is obtained by further pressing or solvent extraction, is more or less colored, and is used only for industrial purposes

The A O C S recommended standard for castor oil is as follows [51]

Specific gravity at 25°/25°C	0 915–0 965
Refractive index at 25°C	1 473 1 477
Iodine value (Wijs)	81–91

[114] K D Guha, T P Hilditch and J A Lovern, *Biochem J*, 24, 266 290 (1930)

Saponification value	176–187
Unsaponifiable matter, %	Not over 1 0
Acetyl value (André Cook)	Not less than 144

The following analysis of a sample of castor oil was reported by Kaufmann and Bornhardt [115]

Iodine value (Kaufmann)	85 8
Saponification value	195 4
Saturated acids	2 4
Dihydroxy stearic acid	0 6
Oleic acid	7 4
Ricinoleic acid	87 0
Linoleic acid	3 1

Castor oil is distinguished from other oils by its high acetyl or hydroxyl value, and from other oils of comparable iodine value by its high specific gravity Unlike other oils, it is miscible with alcohol, but is only slightly soluble in petroleum ether at room temperatures It is much more viscous than other oils (see pages 53–55), and when completely hydrogenated has an abnormally high melting point (86–88°C) The titer of castor oil is lower than that of any other common oil

[115] H P Kaufmann and H Bornhardt, *Fette u Seifen*, 46, 444–446 (1939)

C. INDUSTRIAL UTILIZATION OF FATS AND OILS

CHAPTER VIII

COOKING AND SALAD OILS; SALAD DRESSINGS

1. Introduction

The oil and fat products which are used for edible purposes may be divided into two fairly distinct classes, namely the liquid oils, such as olive oil, and the plastic fats, such as butter and lard In the preparation of some foods it is of no particular consequence whether the fatty material used is liquid or solid, but in certain others the consistency of this material is a matter of great importance For example, in the preparation of a green salad, the object is to provide an oily coating for the various ingredients of the mixture For this purpose, a liquid oil must be used, a plastic fat, such as butter or lard is entirely unsuitable On the other hand, it would be impossible to use a salad oil in the place of a plastic fat in making a pound cake The leavening of such a cake depends entirely upon the air that can be whipped into the fat contained in it, and air cannot be incorporated into a liquid oil

For reasons related to both history and climate, there are decided geographical divisions of fat and oil consuming peoples The forebears of the present inhabitants of central and northern Europe derived their edible fats almost wholly from domestic animals Consequently, the food habits and cuisine of these people were developed around the use of plastic fats, and butter, margarine, lard, and shortenings continue to be their principal fatty food materials

On the other hand, in the older civilizations of southern Europe, northern Africa, the Near East, and the Orient, the pressure of population has long since made the extensive raising of livestock impractical, and has required the edible oils of these regions to be derived principally from intensively cultivated vegetable crops In the more tropical regions of the globe, conditions are relatively unfavorable for livestock production, but are extremely well suited to the culture of certain oil bearing plants, some of which flourish in the wild state

Oil-bearing plants all yield liquid oils or oils which like that of the coconut are normally liquid at the temperatures generally prevailing where the plant grows The native cuisine of peoples accustomed to these oils naturally does not include preparations requiring the use of plastic fats

In the New World, plastic fats are the most widely used edible materials, because of the predominantly northern European extraction of the earlier

North American settlers, and the fact that large sections of both North and South America are eminently adapted to the large scale raising of domestic animals

There is probably in general a somewhat greater utilization of liquid oils in the countries which largely consume plastic fats than of plastic fats in oil consuming regions This is in part due to the relatively greater heterogeneity of the population in some of the former, notably in the United States, and in part to the generally more cosmopolitan cuisine of the more highly industrialized countries

2 Consumption of Salad and Cooking Oils

Liquid oils are in general suitable for all classes of cooking except those which require the production of a highly developed dough structure They are, of course, unsuitable as spreads for bread or for the production of plastic products such as cream icings or fillings

In a typical meal prepared with plastic fats, the various meat and vegetable dishes will be relatively low in fat content, and a large part of the total fat in the food will be in the form of butter or margarine, to be spread on bread In a typical meal containing only liquid oils, there will be no spread for the bread, but the meat and vegetable dishes will be enriched by sauces and gravies of high oil content

In addition to their household and restaurant uses, cooking oils are in considerable demand for commercial deep frying, particularly for products such as doughnuts which are consumed reasonably soon after their preparation For frying potato chips and similar packed products which must be able to withstand considerable periods of storage, plastic hydrogenated oil products are generally preferred, because of their greater stability

Cooking oils are also used in some quantity for packing certain canned meat and fish products, including sardines anchovies and sausages

All cooking oils are vegetable products The only liquid animal oils are of marine origin (chiefly whale and fish oils), and these oils, because of their high degree of unsaturation, are in most parts of the world not considered edible in their natural form They are edible after hydrogenation and deodorization but then are, of course, fats rather than oils

In the United States there is a rather sharp differentiation between cooking oils and salad oils The latter term is applied to oils which will remain substantially liquid in a refrigerator at 40° to 45°F , and produce a mayonnaise emulsion which is stable at low temperatures

The labeling of an oil simply as a cooking oil implies that it is not a salad oil, and hence is either peanut oil or unwinterized cottonseed oil Both of these oils congeal at the above mentioned temperature Much the greater part of the finished edible oils sold in the United States are labeled and marketed as salad oils, regardless of their intended uses

Exact figures on the production and consumption of salad and cooking oils in the United States in past years are not available However, the Bureau of the Census has reported the annual factory consumption of various fats and oils in the manufacture of edible products other than shortening and margarine Since cottonseed, corn, soybean, peanut, and sesame oils are little used in confections or other miscellaneous edible products, their combined consumption outside of shortening and margarine approaches quite closely the amount actually going into cooking and salad oils and salad dressings The factory consumption of these oils, together with the consumption of edible olive oil in recent years in the United States,[1] is shown in Table 88 Beginning with the second half of 1942, reports

TABLE 88

CONSUMPTION IN THE U S IN MILLION POUNDS OF EDIBLE OLIVE OIL AND FACTORY CONSUMPTION OF CERTAIN OTHER OILS IN EDIBLE PRODUCTS OTHER THAN SHORTENING AND MARGARINE[a]

Year	Cotton seed	Corn	Soybean	Peanut	Sesame	*Total* of oils other than olive oil	Olive oil	*Grand total*
1931	84 4	20 3	0 0	1 4	0 1	106 2	76 3	182 5
1932	100 1	27 3	0 2	1 2	0 1	128 9	74 5	203 4
1933	121 5	27 9	0 5	1 3	4 8	156 0	71 8	227 8
1934	155 3	38 6	0 5	0 9	1 4	196 7	62,1	258 8
1935	138 6	36 1	9 4	3 6	14 6	202 3	70 3	272 6
1936	178 3	51 0	21 6	2 4	16 7	270 0	64 4	334 4
1937	226 6	63 9	15 5	3 2	3 4	312 6	52 3	364 9
1938	198 1	57 1	11 3	1 9	1 6	270 0	73 3	343 3
1939	233 4	65 4	32 3	8 7	1 1	340 9	65 8	406 7
1940	263 3	71 0	40 0	9 7	1 1	385 1	52 8	437 9
1941	311 6	63 0	48 0	18 1	0 3	441 0	22 0	463 0

[a] Figures for cottonseed corn soybean peanut, and sesame oils from U S Bur Census *Animal and Vegetable Fats and Oils* Figures for olive oil from U S Dept Agr B A E , *The Fats and Oils Situation* November 1942

have been made of the actual consumption in salad and cooking oils and salad dressings The factory consumption in these products for the year beginning July 1, 1942, is shown in Table 89

Salad and cooking oils are of two different kinds, which consist respectively of naturally flavored oils, and neutral, deodorized products Olive oil is invariably marketed in the undeodorized form In olive oil, as in butter, the natural flavor of the product is an important asset It is principally because of its distinctive and highly prized flavor that olive oil is generally more expensive than other vegetable oils

The vegetable oils other than olive oil may or may not be processed for flavor removal, depending upon local taste and custom In the Orient the common cooking oils, such as soybean, peanut, rapeseed, sunflower,

[1] U S Dept Agr B A E *The Fats and Oils Situation* November 1942

and sesame oil are generally consumed in their crude form, as expressed from the oilseeds In Occidental countries, however, it is the more general practice to subject these oils first to refining and deodorizing treatment

One reason for the general practice of deodorizing vegetable oils in Europe and North and South America is the relative unfamiliarity of the people of these regions with natural oil flavors The movement of edible vegetable oils from Africa and Asia to Europe and America has grown to large proportions in the past few decades, but the bulk of this oil has been manufactured into margarine or shortening, rather than consumed in the

TABLE 89

FACTORY CONSUMPTION IN MILLION POUNDS OF VARIOUS OILS IN THE MANUFACTURE OF COOKING AND SALAD OILS AND SALAD DRESSINGS IN THE U S DURING THE YEAR BEGINNING JULY 1, 1942[a]

Oil	Cooking and salad oils	Mayonnaise and salad dressings
Cottonseed	375 2	110 4
Corn	10 2	94 4
Soybean	72 8	19 9
Peanut	11 9	—
Other vegetable oils	2 0	—
TOTAL	472 1	224 7

[a] U S Bur Census, *Animal and Vegetable Fats and Oils*

liquid state Since oils must be processed for flavor removal before they can be used in either of these products, this movement has done little to accustom Americans and Europeans to the natural taste of the foreign oils

In the United States, deodorized oils are in particular demand The only vegetable oil consumed in the United States for many years was cottonseed oil, which is so strongly and unpleasantly flavored that processing treatment is absolutely necessary to render it edible The wide scale sale of neutral cottonseed oil products over many years has developed a general preference for odorless and tasteless fats in this country which appears to be growing yearly The relative decline in importance of olive oil as an edible oil in the United States during the past several years is evidenced in the figures of Table 88 While the consumption of olive oil has remained virtually stationary over a ten year period, the consumption of other vegetable oils in products consisting largely of cooking and salad oils has increased fourfold

Another reason for the practice of deodorizing edible oils for consumption in European and American countries relates to the different quality of the oil obtained by Oriental and Occidental methods of extraction In

such countries as India and Chma, edible oils are principally produced in small, relatively crude mills, by expressing the oilseeds at low pressures and without previous heat treatment A low yield of oil is obtained by such methods but a minimum amount of nonoil substances is expressed from the seed, and the oil is consequently of relatively mild flavor and odor

In the mdustrial nations of the Occident, the extraction of oil from oilseeds is carried out in large factories These factories handle a great volume of material and operate on a highly competitive basis Naturally every effort is made to obtain the greatest possible yield of oil from the oil bearing materials Very high pressures are used in expressing the oil, and in order to improve the efficiency of extraction the oilseeds are cooked or given a heat treatment before they are pressed In some cases extraction by means of solvents is substituted for mechanical expression By such methods the quality of the oil is in no wise impaired, insofar as its stability or its nutritive qualities are concerned, but it has a stronger flavor and odor than oil prepared by low pressure expression of uncooked seeds The expense of refining and deodorizing the oil to render it palatable is more than compensated by the greater amount of oil obtained

3 Olive and Other Naturally Flavored Oils

The manufacture of olive and other naturally flavored salad and cooking oils requires nothing more than extraction of the oil from the oil bearing materials, clarification of the extracted oil by filtration or settling, and packaging of the resultant product

The more popular brands of olive oil are blends of oil from a number of different sources The quality and flavor of olive oil varies considerably from one season and one locality to another, and in order to turn out a product of more or less uniform characteristics, it is necessary for the packer to have access to a variety of oils

There is a considerable sale of "virgin," cold pressed oils such as peanut, sesame and sunflowerseed in many European countries, as well as in the Far East, but in the United States the sale of undeodorized vegetable oils other than olive oil is virtually nil

The relative consumption of olive oil in different countries has been discussed on pages 112–113 The annual world consumption is in the neighborhood of 2,000,000,000 pounds There is no way of estimating the quantities of soybean, peanut, palm, coconut, sesame, sunflower, rapeseed, and minor oils which are annually consumed in an unprocessed form in different parts of the world, but the total is undoubtedly large

4 Neutral Cooking Oils

Deodorized cooking oils are principally prepared from cottonseed, peanut, sunflower, sesame, corn, soybean, and rapeseed oils Of these oils,

the five first mentioned may be considered the most choice, as all may be converted to bland, neutral products, which do not readily deteriorate in flavor Soybean oil is subject to a characteristic reversion to a slight "beany" flavor, which invariably occurs almost immediately after the oil is deodorized This flavor is not objectionable to all consumers, but it has the effect, none the less, of somewhat limiting the use of this oil as a salad and cooking oil Deodorized rapeseed oil also has a characteristic flavor reversion

The processing treatment required for converting crude oils to neutral cooking oils is relatively simple The oil is first refined, usually with caustic soda If the color of the finished oil is not critical, the oil is then deodorized without bleaching If a very light colored oil is desired, the oil is bleached with fuller's earth before it is deodorized

The standard packages for cooking oils in the United States are 55-gallon steel drums, and 5 gallon, 1 gallon, 1 quart, and 1 pint tin cans Glass containers are sometimes substituted for the smaller sized cans, but are less desirable than tins, because they do not protect their contents from the deteriorative influence of light If cans are filled very full of oil, to eliminate oxygen in the head space, and are sealed airtight, the oil will keep for long periods at ordinary temperatures

5. Neutral Salad Oils

As mentioned previously, most of the neutral oil sold in the United States is actually salad oil, rather than cooking oil, the difference between the two being that salad oil will not solidify at temperatures of 40° to 50°F, whereas cooking oil may do so The preference for salad oils in this country is principally due to the widespread use in the home of mechanical refrigerators, which provide a food storage temperature of 40° to 45°F An oil which becomes solid in the refrigerator is inconvenient to handle, as it will not pour from its container In addition, a mayonnaise salad dressing made from such an oil and kept in the refrigerator will suffer a breakdown of its emulsion due to crystallization of the oil

Refined sesame, sunflower, corn, and rapeseed oil all remain liquid naturally at low temperatures, hence in the case of products prepared from these oils there is no distinction between salad oils and cooking oils Cottonseed oils must be subjected to "winterization," for removal of its higher melting glycerides, before it may be classified as a salad oil Soybean oil and some corn oils deposit a small quantity of wax upon chilling, which must be removed if a product is to be obtained which will remain perfectly clear at low temperatures Peanut oil, because of its tendency to deposit very difficultly filterable crystals, is not winterized commercially, and hence is not marketed as a true salad oil, but only as a cooking oil

The relative popularity of different oils for salad and cooking oil manufacture is evident from Table 89

Almost all the corn oil available is made into salad and cooking oils The large use of corn oil for this purpose is partly due to the fact that it requires no winterization, and partly due to its rather dark natural color, which is undesirable in shortening and margarine The relatively slight use of soybean oil is due to its tendency to revert in flavor Sesame and sunflower oils are both excellent naturally winterized salad oils, but are not normally available in any considerable quantities in the United States

The procedure followed in manufacturing salad oils does not differ from that employed for making cooking oils except in the case of cottonseed oil, which must be winterized Winterization is always carried out after refining and bleaching but before deodorization

The extent to which salad oils are bleached depends to some extent upon the trade for which they are designed The brands of cottonseed salad oil which are most popular for home use in the United States are quite light, with Lavibond red colors of 1 5 to 2 5 units However, a certain class of trade, particularly that accustomed to the rather dark color of olive oil, prefers a more strongly colored oil For this trade, an oil is manufactured with a red color of 4 0 to 6 0 units Refined, unbleached cottonseed oil becomes considerably lighter with deodorization, and for the production of dark salad oils it may be necessary to specially refine the crude oil with the object of producing an abnormally dark refined oil For commercial mayonnaise and salad dressing manufacture a dark colored oil is acceptable, as a yellow color is desired in the finished product

The standard method of evaluating the winterization of salad oils is the cold test of the American Oil Chemists' Society The oil sample, in a sealed 4-ounce bottle, is placed in a bath of melting ice at 32°F If it remains clear at the end of 5 5 hours, it is considered a suitably winterized oil Most cottonseed salad oils, however, will remain clear for 8 to 16 hours and an exceptionally well winterized oil may have a cold test of 24 hours or longer From a practical standpoint the number of hours required for the oil to cloud is of less significance than the character and amount of the crystals deposited after a prolonged period of storage, at 32°F , or higher Some oils may cloud quite readily, yet remain in a fluid condition for an extended period of time Others may be relatively slow in clouding, but thereafter may quickly become semisolid or solid

The pour points and solidifying points of salad oils, as determined by the A S T M method for mineral oils, are also an indication of the extent to which an oil will withstand low temperatures Cold tests, pour points, solidifying points, and other analytical data on typical samples of commercial salad oils are given in Table 90

TABLE 90

ANALYSES OF TYPICAL COMMERCIAL SAMPLES OF SALAD AND COOKING OILS

Analysis	Olive oil	Salad oil (corn oil)	Salad oil (soybean oil)	Salad oil (winterized cottonseed oil)	Salad oil (winterized cottonseed oil)	Cooking oil (cottonseed oil)	Cooking oil (peanut oil)
Iodine value	85 0	125 0	132 0	112 0	111 5	108 0	95 0
Refractive index at 60°C	1 4546	1 4598	1 4602	1 4577	1 4576	1 4572	1 4550
Free fatty acids per cent as oleic	1 5	0 05	0 02	0 02	0 02	0 03	0 03
Smoke point °F	—	420	450	450	450	440	440
Keeping quality, Swift method, hrs to peroxide, value of 125	20	10	8	10	10	10	12
Color, Lovibond	—	35Y-6 0R	15Y-1 8R	15Y-1 5R	35Y-4 5R	20Y-2 5R	15Y-1 5R
Flavor and odor	Characteristic	None	Slightly beany	None	None	None	None
Cold test, hrs to cloud at 32°F	Over 24	Does not cloud	Does not cloud	14	10	<1	<1
Pour point, A S T M °F [a]	22	12	14	24	26	38	40
Solid points, A S T M, °F [a]	14	8	10	20	22	28	34
Titer, °C	23 0	18 5	21 5	33 0	33 2	36 0	31 3

[a] Modified by examination of sample at intervals of 2°F rather than 5°F

Salad oils are packaged in the same containers as cooking oils Manufacturers of mayonnaise and other large users of oils purchase their oil in 55 gallon drums or tank cars The oil packaged in 1 gallon and 5 gallon cans goes principally to restaurants and hotels The most popular household packages are 1 quart and 1 pint cans

6 Salad Dressings[2]

(a) *Mayonnaise*

According to the definition officially adopted in 1931 by the U S Food and Drug Administration mayonnaise consists of the following

> The semisolid emulsion of edible vegetable oil egg yolk or whole egg a vinegar and/or lemon juice with one or more of the following salt other seasoning commonly used in its preparation sugar and/or dextrose The finished product contains not less than 50% of edible vegetable oil

Actually, the ingredients of mayonnaise are almost always cottonseed or corn oil, vinegar, egg yolk, sugar, salt, mustard, and white pepper Although mayonnaise may legally contain as little as 50% of oil, the usual content is between 70% and 80% The consistency of the emulsion depends to some extent upon the volume ratio of its aqueous and oil phases and it is difficult to produce a mayonnaise with a sufficiently stiff body with less than this proportion of oil Also, the use of a low percentage of oil necessitates the use of a relatively high proportion of egg yolks, which are normally more expensive than the oil Two typical formulas for mayonnaise are the following (all ingredients in terms of per cent by weight)

Ingredient	Formula A	Formula B
Oil	75 00	80 00
Vinegar (4 5% acetic acid)	10 80	9 40
Egg yolk	9 00	7 00
Sugar	2 50	1 50
Salt	1 50	1 50
Mustard	1 00	0 50
White pepper	0 20	0 10

The color of mayonnaise is a pale creamy yellow The color derives mainly from the egg yolks used in its manufacture, rather than from the oil

Physically, mayonnaise consists of an internal, or discontinuous phase of oil droplets dispersed in an external or continuous aqueous phase of vinegar, egg yolk, and other ingredients The vinegar, sugar, salt, and spices largely determine the flavor of the product The egg yolks also

[2] For a general discussion of these products including methods of analysis see the monograph by M H Joffe *Mayonnaise and Salad Dressing Products* The Emulsol Corporation, Chicago, 1942

contribute to the flavor, but their chief function is that of an emulsifying agent[3]

In making mayonnaise it is generally desired to produce as stiff an emulsion as possible When mayonnaise is made up according to a given formula, the stiffness of the emulsion is principally determined by the degree of subdivision attained in the individual oil droplets In a good mayonnaise emulsion, the largest droplets will not be more than 6 to 8 microns in diameter and many will be in the range of 2 to 4 microns In poor emulsions, most of the droplets may be 10 microns in diameter, or larger Usually about 10% to 12% of air, by volume, is incorporated into the emulsion during the mixing operation

All mayonnaise gradually becomes thinner with age, due to gradual coalescence of oil particles, and if kept for a sufficient length of time, will eventually separate more or less completely into two separate phases The thinning and separation of mayonnaise is greatly accelerated by mechanical shock or vibration, such as occurs in shipment of the product As stated previously, the emulsion will also be broken if it is subjected to temperatures low enough to cause extensive crystallization of the oil

Mayonnaise may be classed as a semiperishable product It is sufficiently stable to keep for reasonable lengths of time without refrigeration, but it will not stand indefinite storage Mayonnaise chiefly becomes unmerchantable, however, from breakdown of the emulsion or from oxidation, rather than from the action of microorganisms whose growth is effectively inhibited by the acidity of the product

Manufacture—Mayonnaise is usually mixed in special machines equipped with removable bowls and beaters, which are similar in design to ordinary baker's cake mixing machines The usual procedure in mixing mayonnaise is as follows (*1*) First, place in the bowl all the egg yolks sugar, salt, and spices and a portion of the vinegar and mix, (*2*) gradually beat in the oil, (*3*) thin out, by mixing in the remainder of the vinegar This method of mixing gives a product of better consistency than is obtained by adding the entire amount of vinegar at the beginning of the operation Gray, Maier, and Southwick[4] have made a study of the effect of the method of mixing on the consistency of the emulsion and recommend that one third of the vinegar be added initially in making mayonnaise containing 78% of oil

The temperature of the oil and other materials during the mixing also influences the body of the mayonnaise A thin product results if the oper

[3] J W Corran has shown that the powdered mustard in mayonnaise also acts as an emulsifying agent and that its effect is antagonistic to the tendency of calcium soaps to reverse the emulsion type See International Soc Leather Trades Chemists *Emulsion Technology* Chem Pub Co New York 1943 pp 176–192

[4] D M Gray, C E Maier and C A Southwick *Glass Packer*, 2 397–400 (1929)

ation is carried out with materials that are too warm Gray and Maier[5] who have investigated this phase of mayonnaise manufacture, suggest a temperature of 60° to 70°F as most suitable They found that the emulsion was increasingly thick with decreased temperatures down to 40°F The lower temperature products lost much of their initial superiority over 60–70° products with slight aging, however, and the inconvenience of at tempting to operate at temperatures below 60°F was not judged to be worth while

Special mixing devices of the colloid mill type have been recommended as being particularly efficacious in producing a fine emulsion, of superior consistency and stability They do not appear to have been widely adopted in the industry, however, possibly due to their relatively high cost and their high power requirements, in comparison with mixers of the con ventional type

Various instruments have been devised for testing the important prop erty of consistency in the mayonnaise emulsion One device in common use is a modified form of the Gardner mobilometer[6,7] which was originally designed for testing paints, varnishes, and enamels The mobilometer is in reality a special form of viscometer in which a weighted plunger equipped with orifices is pressed through the sample Another suitable device is a special orifice type viscometer which utilizes air pressure rather than gravity to discharge the sample through a standard orifice Kilgore[8] has de vised a simple method which is particularly suitable for control work, since it involves nothing more than dropping a pointed rod or "Plumit" into a sample from a definite height, and noting the depth of its penetra tion

The ability of a mayonnaise emulsion to resist mechanical shock is commonly evaluated by testing samples for a prolonged period in a labora tory shaking machine

The suitability of different varieties of oil for mayonnaise manufacture has been discussed in a previous paragraph (page 194) The best mayon naise oils are corn oil, sunflower oil, sesame oil, and well winterized cotton seed oil Only the best grades of the different oils should be used Mayonnaise manufacturers usually specify that oils should be low in free fatty acid content (*e g*, not over 0 03%), completely neutral in flavor and odor, and free from any trace of reaction in the Kreis test The vinegar and spices used in mayonnaise do not serve, as one might suppose, to suppress or disguise the flavors of poorly deodorized or partially oxidized oils They have the effect, rather, of accentuating any flavor that the oil may

[5] D M Gray and C E Maier, *Glass Packer*, **4**, 23 25, 40 (1931)
[6] H A Gardner and A W Van Heuckeroth *Ind Eng Chem* **19**, 724 726 (1927)
[7] D M Gray, and C A Southwick *Glass Packer*, **2**, 17–19, 42 77–81 (1929)
[8] L B Kilgore, *Glass Packer*, **4**, 65–67 90 (1930)

possess For this reason, more strict neutrality is required in a mayon naise oil than in almost any other oil or fat product

Consumption —The growth of the mayonnaise industry in the United States in the past 20 years has been extremely rapid A survey conducted by the U S Department of Commerce in 1929 indicated a consumption of oil in mayonnaise and salad dressings during that year of about 100 000 000 pounds It is certain that the consumption of mayonnaise has in creased very greatly since that time In fact, it is probable that the ap proximately fourfold increase in the production of neutral oils from 1931 to 1941 (see Table 88) is for the most part due to the demand for these products for the manufacture of salad dressings and mayonnaise

Although mayonnaise was originally nothing more than a dressing for salads, it has lately been adopted and used in large quantities for an en tirely different purpose, namely, as a spread for bread As mayonnaise consists largely of oil, it may be said that the manufacture of mayonnaise actually represents a method for converting a liquid oil to a plastic product competitive with butter

Vast quantities of mayonnaise are now used in the United States in sandwich stands, drug stores, and the home, for supplying the spread of fat which is considered essential in the preparation of sandwiches For commercial use in sandwich making, mayonnaise has in fact almost com pletely replaced butter and margarine To the commercial user, mayon naise recommends itself as a sandwich ingredient in a number of different ways It has considerable flavor of its own, and it readily blends with a minimum amount of other, more expensive ingredients to form an accept able sandwich filling It is less perishable than butter or margarine Also it is mobile, and easily handled and spread, under all conditions of use

(b) *Other Salad Dressings*

In the grocery trade in the United States, the term "salad dressing" without qualification as to type or variety of dressing, refers to a product which is similar in appearance to mayonnaise but which contains insuffi cient oil to form a true emulsion It is stiffened by the addition of a cooked starch paste Salad dressings are used for the same purposes as mayon naise but are much less expensive

The essential ingredients in a salad dressing are eggs, vinegar, oil starch, and spices The oil content of salad dressings is extremely variable, but ranges usually from about 30% to 50% A formula which is perhaps more or less representative of dressings of reasonably high oil content is given by Campbell[9] as follows (in oz) corn starch, 5 25, water, 80 0, salt, 2 125, vinegar, 10 0, mustard, 0 75, cayenne pepper or paprika dash, egg yolk, 13 33, and oil, 80 0 A cooked paste is prepared from the starch,

[9] C H Campbell, *Canning Age*, 14, 316 (1933)

water, and salt The remaining ingredients are mixed as in the manufacture of mayonnaise, and then blended with the cooled paste

The consistency of salad dressings depends upon the structure of their hydrated starch base In order for the product to simulate mayonnaise it must be semisolid, but it must not develop a continuous gel structure The oil in the dressing is important in preventing gelation, and the extent to which the oil content may be reduced is limited by the danger of gel formation

There are a number of other prepared salad dressings on the market in the United States, but the volume of sales of these is unimportant in comparison with that of mayonnaise and salad dressing A number of these dressings, and also certain "sandwich spreads," etc , utilize a mayonnaise or salad dressing base

CHAPTER IX

PLASTIC SHORTENING AGENTS

1. Definition of Plastic Shortening Agents

The materials which are herein designated as plastic shortening agents comprise lard and those products of lardlike consistency which have come to be known as shortenings They consist of pure fat, unmixed with other substances, and are distinguished here from leaf fat, salt pork, suet, or other fatty animal tissues, and from butter or margarine, which are mixtures or emulsions of fat and an aqueous liquid

2 Historical

Some knowledge of the history of the lard and shortening industries is essential to a full understanding of the problems involved in the technology of their products Therefore, before proceeding to a description of the individual products a brief review will be presented of the development of these industries For additional details regarding the history of the shortening industry the reader is referred to the monograph on this subject by Weber and Alsberg[1]

The first oil or fat products used by man undoubtedly were rendered from the carcasses of wild animals As animal husbandry became generally practiced, in a more advanced state of civilization, the body fat of domestic animals came to be an important article of commerce In addition to their use as edible materials, animal fats found a wide variety of other applications, as for example, as illuminants, lubricants, and materials for making soaps Wild animals ceased to be an important source of fats at an early date However, with the development of the whaling and sealing industries, the supply of domestic animal fats was supplemented by large quantities of marine oils of analagous origin

As the various uses of fats became more highly specialized and standardized, the body fat of hogs, or lard, came to be the preferred fat for edible purposes, whereas the other animal fats were utilized principally in nonedible products This particular trend of specialization may have been in part due to the distinctive flavor of lard, which possibly is inherently more pleasing than that of beef or mutton tallow or marine oils The chief reason, however, for the favor enjoyed by lard as an edible fat is

[1] G M Weber and C L Alsberg *The American Vegetable Shortening Industry* Food Research Institute Stanford University, 1934

undoubtedly the particular consistency of this fat At ordinary temperatures, lard has very nearly the optimum consistency for the readiest and most efficient incorporation into breads, cakes, pastries, and other leavened baked products Tallow is too firm for this purpose, except at quite elevated temperatures, and marine oils are too fluid

For many years, lard and other animal fats have not been primary products of animal husbandry, but merely by products of the meat packing industry The extent to which lard is produced now depends purely upon the demand for pork Consequently, the supply of lard is not directly related to the demand for this commodity

For some time the production of lard has been far short of the demand for plastic shortening agents in the lard consuming countries This has stimulated the production and use of both vegetable and marine oils, which are now consumed in large quantities in the American and European countries which formerly depended almost entirely upon animal sources for their edible fats

Since the people of these countries were accustomed to the use of plastic fats rather than liquid oils, it was natural for the manufacturers of food products to seek means of converting the vegetable and marine oils to plastic products Originally this was accomplished by blending a relatively large proportion of vegetable oil with a relatively small proportion of oleostearine or other very hard animal fat Later the method of hardening oils by catalytic hydrogenation was developed This process enabled the manufacturer to produce a plastic product entirely from a liquid vegetable oil, and also made it possible to produce shortenings and margarine from marine oils

In Europe, the vegetable and marine oils are principally made into margarine, which is designed to have as nearly as possible the characteristics of butter In the American countries, however, and particularly in the United States, the tendency has been rather to utilize these oils in the form of shortenings which more or less simulate lard

Shortening is an American invention, growing out of the cotton-raising industry The rapid expansion in the acreage of cotton grown in the United States, between the end of the Civil War and the close of the 19th century, resulted in large quantities of cottonseed oil being produced, as a by product of the growing of cotton for lint Shortenings were developed to provide an outlet for this oil

The first shortenings were prepared by blending refined and deodorized cottonseed oil with sufficient oleostearine or other hard animal fat to stiffen it to the approximate consistency of lard Such shortenings were termed "lard compounds" or simply "compounds" They were frankly conceived and marketed as substitutes for the more desirable and expensive lard In the development of the shortening industry, the large American meat

packers played a prominent role because of the circumstance of their controlling the output of hard animal fat which was an essential ingredient of the product All the larger packers entered the field in order to market their tallow and oleostearine to the best advantage A large proportion of the shortening manufactured continues to be made by meat packing companies, in spite of the fact that a large part of their product is now of purely vegetable origin

The introduction of the catalytic hydrogenation process into the United States, in about 1910, made the shortening manufacturer independent of the meat-packing industry, and initiated a new era in the manufacture of shortening Thenceforth, the development of vegetable shortenings followed two divergent courses The meat packers continued to manufacture shortenings of the compound or blended type, employing the hydrogenation process only for the manufacture of highly hardened oil or vegetable stearine, to serve as an occasional substitute for oleostearine Since the packers were engaged in the shortening business purely as a sideline, and since the new shortenings were to some extent competitive with lard, it was natural that they were inclined to offer shortenings only as lard substitutes

Other manufacturers of shortening, however, were prepared to exploit the possibilities of the new product to the fullest possible extent, and in consequence, to offer lard the most aggressive kind of competition The early manufacturers of purely vegetable shortening were sufficiently far sighted to abandon the concept of shortening as a mere lard substitute and to immediately offer their product as a new food material, with properties frankly different from the traditional properties of lard The terms "lard compound" and "compound" were dropped and replaced by proprietary names which were not suggestive of any animal product

In addition to conducting an active advertising campaign, the vegetable shortening manufacturers were also active in devising methods for improvement of their product The crude cottonseed oil was more carefully refined and bleached than had been the general custom in the manufacture of compounds New methods of deodorization involving the use of high temperatures and high vacua resulted in the removal of every trace of odor or flavor from the fat Improved methods of solidifying, filling and packaging the product were devised, to enhance its appearance and keeping quality

One of the largest manufacturers of shortening adopted the practice of hydrogenating the entire mass of oil to the desired consistency, rather than stiffening the liquid oil by the addition of a small proportion of highly hydrogenated material This method of manufacture resulted in a product of considerably lower iodine value than ordinary blended shortening and one of consequently improved stability Subsequent improvements in

the technique of hydrogenation enabled manufacturers to steadily reduce the iodine value of their shortening and increase its resistance to oxidation The average iodine value of the first all hydrogenated shortening was in the neighborhood of 80, this was reduced to 75, then to 70, then to 65, and eventually to 60, or slightly above The superior neutrality, stability, and uniformity of the all hydrogenated type of shortening found particular favor with commercial bakers Eventually all of the shortening manu-

TABLE 91

PRODUCTION, EXPORTS, AND PRICES OF LARD COTTONSEED OIL AND SHORTENING IN THE U S (1920–1941)[a]

Year	Production million pounds			Lard exports million pounds	Average prices during January of the year indicated cents/lb		
	Crude cottonseed oil	Shortenings all types	Lard		Crude cottonseed oil (tanks)	Compound type shortening (tierces)	Lard (loose)
1920	1309	747	1943	635	19 7	25 2	22 6
1921	930	811	2092	893	6 1	12 4	11 8
1922	1003	784	2283	787	7 2	11 0	9 4
1923	980	751	2692	1060	9 8	13 4	10 8
1924	1404	830	2635	971	9 5	14 2	11 6
1925	1617	1153	2133	708	9 5	14 7	15 2
1926	1888	1141	2185	717	9 8	13 8	14 2
1927	1477	1179	2240	702	6 9	10 7	11 5
1928	1604	1143	2432	783	8 5	12 9	11 0
1929	1572	1220	2435	848	8 6	12 4	10 9
1930	1442	1211	2201	656	7 2	10 8	9 5
1931	1694	1171	2280	578	6 2	9 4	7 9
1932	1446	945	2353	552	3 2	6 3	4 6
1933	1303	953	2448	584	2 9	5 3	3 6
1934	1109	1204	2068	435	3 6	7 0	4 6
1935	1164	1547	1270	97	9 6	13 1	12 5
1936	1364	1587	1676	112	8 9	12 4	10 6
1937	1961	1595	1417	137	10 4	13 7	12 8
1938	1409	1514	1713	205	6 2	10 2	8 2
1939	1325	1404	1998	277	6 0	9 2	6 3
1940	1356	1190	2297	201	5 9	9 5	5 3
1941	1391	1418	2250		5 4	10 3	5 6

[a] Data compiled from U S Bur Census *Animal and Vegetable Fats and Oils* 1938 to 1942 Washington 1943 from U S Dept Agr, *Agricultural Statistics* 1942 and from publications of the Bureau of Agricultural Economics of the U S Department of Agriculture

facturers, including the meat packing companies, took up the manufacture of shortening of this variety for their baking trade, even though many continued to make only shortenings of the compound type for household consumption

In the long standing competition between lard and vegetable shortening, lard appears at present to be at a rather decided disadvantage Certain statistical data relative to the production and consumption of lard, cottonseed oil, and compound-type shortenings in recent years in the United

States are recorded in Table 91. The prices listed in this table for the three fats are not strictly comparable. The cost of solidifying the fat and placing it in containers (tierces) is included in the price of compound shortening, whereas crude cottonseed oil and lard are quoted on a loose basis The tiercing cost amounts to approximately one cent per pound. However, it will be seen that by 1920, compound shortening had attained a virtual parity in price with lard. Shortenings of the all-hydrogenated variety have at all times commanded a price substantially above that of compounds. The approximate parity in price between lard and compound shortening persisted for a number of years, during which the total production of lard amounted to between 2 and 2.5 billion pounds, of which about one-third was regularly exported.

Following the business recession beginning in 1929, exports of lard decreased, with the result that the price of lard dropped somewhat more drastically than that of compounds or cottonseed oil. By 1935, governmental control had restricted the production of both lard and cottonseed oil, and almost eliminated the former from export trade. The restriction of lard production was more severe than that of cottonseed oil, and was less quickly recovered after the relaxation of control measures. Consequently, until lard production again became normal, in about 1939, the price of lard again followed closely the price of compound shortenings.

In 1939, the production of lard again approached 2,000,000,000 pounds but exports lagged at less than 300,000,000 pounds. The price of lard then fell far below that of compounds and closely approached that of the crude cottonseed oil from which these shortenings are principally manufactured By late 1941, when prices of fats and oils were stabilized by governmental action, the price of prime steam lard in tierces at Chicago was 1.4 cents per pound under that of crude cottonseed oil in tank cars at the mills. Subsequent shipment of government purchased lard to Europe in large quantities increased the demand for this product, and resulted in the ceiling price of lard being raised to approximately that of cottonseed oil. The government controlled wholesale prices prevailing in January, 1943, for lard, shortenings, and certain raw materials for shortening manufacture were as follows (in cents per pound):

Lard, loose, Chicago	12.80
Lard, prime steam, tierces, Chicago	13.80
Lard, refined, cartons, Chicago	15 55
Animal fat compounds, cartons, Chicago	17.19
Hydrogenated shortenings, cans or jars	21.50
Oleostearine, prime, barrels, Chicago	10 61
Tallow, edible, tanks, Chicago . . .	9 875
Cottonseed oil, crude, tanks, mills	12 75
Cottonseed oil, refined, tanks, New Y	13 95
Peanut oil, crude, tanks, mills	13.00
Soybean oil, mills	11.75

The high degree of favor enjoyed at present by the vegetable shortenings is doubtless due in part to their superior physical properties, as compared with lard Much American lard is not only rather softer in consistency than is desirable, but is also nonuniform in consistency, due to variations in composition according to the feed of the hogs, and other factors Also, lard does not cream well in the manufacture of cakes and sweet goods, and is much less resistant to deterioration through oxidation than good vegetable shortening Good creaming and mixing properties, high stability, and uniformity, are properties which are particularly desired by commercial bakers The increased use of shortening agents in baked goods in recent years has caused a relative increase in the demand for shortenings

Another property of lard which now appears to be rather more of a liability than an asset is its distinctive flavor Through the prolonged use of odorless and tasteless shortenings and cooking oils, a large and apparently growing segment of the American people has developed a distaste for all natural fat flavors save that of butter If there is a continuation of the present trend toward the consumption of neutral fat products, it appears not unlikely that, in the United States, lard, like the crude vegetable oils, may eventually constitute merely a raw material for the manufacture of edible products, rather than a primary edible material This possibility is given color by recent small scale production, by different packers, of lard products which have been refined, hydrogenated, and in some cases fortified with antioxidants, to give them some of the desirable properties of vegetable oil shortenings

3 Plasticity in Fats

(a) Physical Structure of Fats

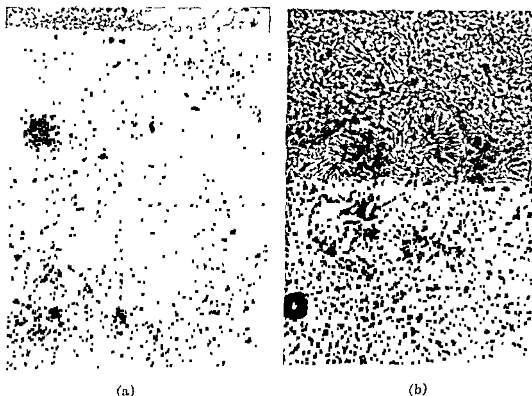
A fat such as lard or shortening is to casual appearance a soft, but more or less homogeneous solid Under the microscope, however, it can be seen to consist of a mass of very small crystals (Fig 11), in which is enmeshed a considerable proportion of liquid oil If the fat is more carefully examined, with the assistance of an apparatus designed for micromanipulation, it will be seen that the crystals are not joined together to form a continuous structure, but that each is a separate and discrete particle capable under the proper shearing stresses of moving independently of the other crystals Thus the fat has the characteristic structure of a plastic solid

(b) Theory of Plasticity

The distinguishing feature of plastic substances is their property of behaving as solids and completely resisting small stresses, but yielding at once and flowing like a liquid when subjected to deforming stresses above a certain minimum value Thus a fat or other firm plastic material will

not flow, collapse, or otherwise deform of its own weight, although it may be easily molded or dispersed into any desired form.

There are three conditions which are essential for plasticity in a material First of all, it must consist of two phases. One of the phases must be solid and the other must be liquid, or else the two must be capable of acting as solid and liquid. In the case of plastic emulsions, the disperse phase may actually be either an immiscible liquid or a gas. However, in their state of extreme subdivision the globules of liquid or gas are so powerfully restricted by the forces of surface tension as to behave as solid particles

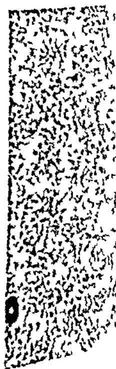


(a) (b)

FIG 11 —Photomicrographs (× 300) of (a) all-hydrogenated cottonseed oil shortening, and (b) hydrogenated lard shortening, both commercially solidified without the incorporation of air

A second condition for plasticity is that the solid phase must be in a state of sufficiently fine dispersion for the entire mass to be effectively held together by internal cohesive forces The solid particles must be small enough for the force of gravity on each to be negligible in relation to the adhesion of the particle to the mass, and the pores or openings between the particles must be so small that there is a negligible tendency for the liquid phase to flow or seep from the material

The third condition for plasticity is a proper proportion between the two phases The solid particles must not be so few that the mass can flow without these particles forming interfering clots and jams On the other hand,



the solid particles must not be so preponderant as to form a locked structure

According to the concept of plasticity developed by Binghai a plastic solid owes its peculiar properties to the tendency of ticles to form jams or arches which support the material ag stresses Thus the application of small stresses (such as the ity) results in no flow or movement When sufficient force break these jams, however the material abruptly yields an occurs

The hardness or firmness of a plastic substance is purely a magnitude of the stress or load required to cause it to yield ar most obvious factor affecting this value is of course, the vc the solid to the liquid phase, the greater the proportion greater is their opportunity to touch and interlock, and the material The limits within which a material will be plastic what upon the shape average size, and size distribution of According to Bingham, in the case of a material whose s approximate the form of uniform spheres the upper limit of t is close to that obtaining in cubical close packing, namely abo volume The lower limit varies considerably with the size o and the character of the material, but is generally within the to 25%

Another factor which influences the firmness of a plastic n size of the solid particles With other factors constant, the become progressively firmer as their size decreases due to i portunity for the particles to touch and increased friction to in causing it to flow

Other factors which may affect both the firmness of the ma solid–liquid ratio within which it is plastic are the degree of n tion of solid particles, and their consequent tendency to for the extent to which the liquid phase lubricates the solid par points of mutual contact, and the rigidity of the particles

It is to be noted that the viscosity of the liquid phase bea relation to the consistency of the plastic product A materia external phase is a viscous liquid is not necessarily firmer t taining a less viscous liquid in the same proportion

(c) *Importance of Plasticity in Edible Fats*

There are a number of fat products in which the property may be regarded as essential One class of such products cc

products in which plasticity is highly important are the fats which are used as shortening agents in baked products When plastic fats are mixed into a batter or a dough, they are capable of being extended to form streaks and films, whereas under like conditions liquid oils can only be dispersed in the form of droplets or globules Fat films naturally lubricate larger surfaces in the dough than do spherical droplets of oil, and thus have a more pronounced shortening effect

In the process of mixing doughs, plastic fats, unlike liquid oils are able to enclose and hold considerable quantities of air In the manufacture of certain baked products, particularly cakes and other goods containing much sugar, the leavening action of this air is very important The subject of plasticity, as related to the baking properties of shortening materials, is discussed at length in another chapter (page 273) devoted to bakery products

(d) Evaluation of Consistency or Plasticity

The consistency of plastic fats is always measured and expressed in arbitrary units There is no standardization whatsoever of the methods or devices used for measuring consistency, and there are virtually as many different systems of consistency evaluation as there are manufacturers of shortening [3]

From the standpoint of simplicity of the instruments and ease and rapidity of making the tests, the penetration technique of measuring consistency has much to recommend it The measuring operation is particularly simple and easily carried out if a penetrometer is used with a needle or other penetrating device which is actuated simply by the force of gravity

In the succeeding pages, consistency will principally be discussed in terms of macropenetrations by the Goddard Hewes penetrometer[4] in the case of commercially solidified materials Where other fats have been examined, or where it has been desirable to solidify the fat in a standard manner and thus make the examination independent of the manufacturer's method of solidification, the micropenetrometer first proposed by Freyer[5] and modified and standardized by Feuge and Bailey[6] has been used for most consistency measurements

(e) Relation of Temperature to Plasticity

Fats, unlike most plastic materials, vary greatly in consistency with changes in temperature, becoming progressively firmer as the temperature

[3] See A D Rich, *Oil & Soap* 19, 54–57 (1942)
[4] W. R Goddard and C K Hewes U S Pat 1 703 270 (1929)
[5] E Freyer, *Ind Eng Chem , Anal Ed* 2, 423–424 (1930)
[6] R O Feuge and A E. Bailey, *Oil & Soap*, 21, 78–84 (1944)

decreases and softer as it increases This is due to their complex constitution All natural fats consist of a considerable number of different glycerides Each individual glyceride has distinctive melting points in the pure state Consequently, there are definite temperatures below which each glyceride tends naturally to be solid and above which it tends to be liquid However, glycerides never occur in a pure form, they are mixed always with other glycerides in which they are to some degree soluble, even at temperatures well below their melting points

The over all effect of having a variety of glycerides of some degree of mutual solubility is the elimination of sharp solidification or melting points There is no temperature of sharp transition from the liquid to the solid phase, or vice versa If a very cold and almost completely solid fat is heated, every small increment in temperature will result in some proportion of fat crystals becoming liquid (see Fig 5, page 57, and Fig 7, page 63) either through melting, or going into solution in fat already molten Upon cooling, the fat undergoes reverse changes until it is completely solidified Thus the consistency of a plastic fat changes more or less smoothly with changing temperature If fats were simple substances, consisting entirely or almost entirely of single compounds, they would of course melt and solidify sharply, like any other class of compounds, and would exhibit none of the properties of plastic products

Fats are considerably inclined to supercool, consequently, if temperature changes are relatively rapid, an equilibrium in the ratio of solids to liquids will prevail only with ascending temperature In order to properly judge the consistency of a fat at a given temperature it is necessary to know something of the previous history of the sample If the temperature of the sample has been constant for some time, or has been raised from a lower temperature, its consistency may be measured with some confidence If, however, the fat has recently cooled from a higher temperature, it will probably be unduly soft, due to a part of its normally solid glycerides remaining in the supercooled liquid form

Except when the fat is supercooled an anomalous relationship between consistency and temperature is observed only under conditions leading to the formation of fat crystals of an unstable polymorphic form The transition from an unstable to a stable form may be very slow Pronounced polymorphism is most likely to be noticed in commercial fats which have been chilled very quickly and then allowed to stand at a relatively low temperature A fat so treated may actually become firmer with a moderate increase in its temperature, due to the transition of unstable glycerides to stable forms of higher melting point Fats of simple constitution are more inclined to exhibit polymorphism than more complex fats Cocoa butter and other fats of the vegetable butter group are particularly inclined to polymorphism If a sample of cocoa butter is quickly

chilled to refrigerator temperatures it may become completely liquid if suddenly heated to 80°F., whereas its melting point may be 90°F. or higher, if it is slowly heated, to allow time for its glycerides to be converted to their stable, higher melting form. Partially hydrogenated oils do not ordinarily exhibit marked polymorphism, but highly hydrogenated oils and blends of these oils with liquid oils almost invariably show a tendency toward this phenomenon.

The expression "plastic range" is often used in connection with edible fat products. The term is employed loosely, and usually refers to the temperature range within which the product exhibits desirable working properties, rather than the range within which it is actually plastic. A lard or shortening is not ordinarily considered plastic, for example, after it has become so soft as to pour from its container, although it may technically be still plastic at this consistency. The lower limit of plasticity is somewhat indefinite, in the popular sense of the term. Properly speaking, it is marked by the point at which the fat becomes brittle and is inclined to crack rather than flow under deforming stresses.

(f) *Relative Proportions of Solids and Liquids in Plastic Fats*

It is impossible to determine the amounts of solid crystals and liquid oil in a plastic fat directly, by separation of the two phases. However, information on the relative proportions of the two phases may be obtained indirectly, by calorimetric or dilatometric means, since the melting of fat crystals is accompanied by an absorption of heat and an increase in volume

Bailey *et al.*,[7] have employed a calorimetric method to estimate the proportions of solid and liquid glycerides at different temperatures in both a natural cottonseed oil and a hydrogenated cottonseed oil of the approximate consistency of shortening or margarine. From the calorimetric data and micropenetration measurements these authors have been able to estimate the percentage of crystals contained by the average all hydrogenated shortening at various temperatures The estimated percentages are as follows:

At temperature of	Per cent crystals
50°F. (10 0°C)	52%
60°F. (15 6°C)	40
70°F (21.1°C.)	30
80°F. (26 7°C)	21
90°F. (32 2°C.)	16

The data of these workers are shown graphically in Figure 12. No high order of precision can be claimed for the values recorded by Bailey and coworkers, for calculations of the amounts of the two phases were made upon

[7] See G. D Oliver, W S Singleton, S S Todd, and A. E Bailey, *Oil & Soap*, 21, 297-300 (1944), and A E Bailey and G D Oliver, *ibid*, 21, 300-302 (1944)

the assumption of a constant heat of fusion of the fat crystals over the melting range Actually, different glycerides have somewhat different heats of fusion The average heat of fusion of glyceride mixtures appears to increase as their unsaturation decreases,[7] hence it is possible that there was a progressive increase in the latent heat of the glycerides melting as fusion of the fat proceeded The estimated percentages of solid glycerides may, therefore, be regarded as maximum values However, it is clear that commercial fats are plastic and workable within a relatively restricted range of solid glyceride content In the case of hydrogenated cottonseed oil, the range appears to be approximately 15% to 45%

(g) *Relation of Crystal Size to Plasticity*

As indicated previously, the consistency of a plastic material is influenced by the size of the solid particles as well as their total volume, the material becomes progressively firmer as the average size of the particles decreases, and softer as their size increases

It is for this reason that "grainy" lard is softer than "smooth" lard, and shortening melted and slowly resolidified is softer than the same product after it is initially solidified on a chill roll or in a Votator In the commercial preparation of both lard and shortening, the fat is ordinarily chilled very rapidly, so that the crystals will be as small as possible The production of fine crystals extends the plastic range of the product, and gives it a smooth appearance Thus commercial methods of manufacture result in shortening products of the maximum degree of firmness

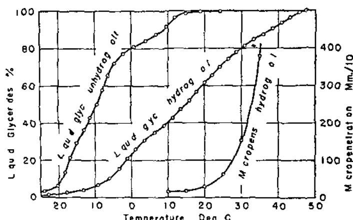


FIG 12 —Estimated per cent liquid glycerides at different temperatures in cottonseed oil and hydrogenated cottonseed oil, and micropenetrations of the hydrogenated oil [7]

The various hydrogenated vegetable oils, and also tallows and tallow derivatives, all form crystals of about an equal size when chilled rapidly Their crystals are so small that it is difficult to form any accurate estimate of their size, but they appear to be of the order of perhaps 2 or 3 microns in length Lard, however, has the peculiar property of solidifying under the same conditions in quite large crystals The characteristically coarse crystal structure of lard is particularly well observed after slight hydrogena-

tion of this fat (Fig 11, page 208) Many crystals of lard are certainly in excess of 20 microns in length If it is assumed that the crystals of lard and hydrogenated lard are 5 times as large in each dimension as those of vegetable shortenings, it follows that the shortening will contain 125 times as many crystals as lard of an equivalent solid glyceride content

In view of the disparity in the size of their crystals, it is interesting to compare the consistencies of shortening and hydrogenated lard containing equal proportions of solid glycerides Such a comparison can be made from Figure 13 It is indicated in the figure that lard must contain about 35% solid glycerides in order to have a consistency corresponding to a macropenetration of 50 mm Hydrogenated cottonseed oil, on the other hand, has an equivalent consistency with a solid glyceride content of but 25% The absolute figures in this example are not significant Calcula-

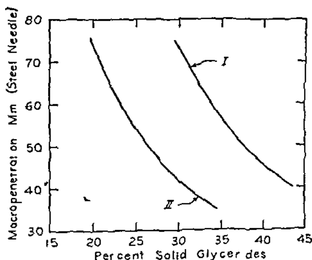


Fig 13 —Solid glyceride contents of hydrogenated cottonseed oil (II) and hydrogenated lard (I) at equivalent consistencies

tions of the amount of solid glycerides were made upon a different basis from those mentioned above, in connection with Figure 12, and the estimated figures are probably in each case too low The data for the two fats are comparative, however, and clearly indicate the greater stiffening effect of the smaller crystals existing in the shortening

(h) *Effect of Temperature Variations in Storage*

In the handling and storage of plastic products subsequent to their solidification, considerable variations in temperature are inevitable Each time that the temperature rises, a portion of the solidified fat becomes liquid, and, as the fat cools, a portion of it again becomes solid If the variation in temperature is at all large, by the time the fat is ready for consumption the greater portion of its solid glycerides may well consist of resolidified crystals rather than the crystals originally occurring in the fat

The cooling which takes place under such conditions is of course very much slower than the cooling applied to first solidify the fat Since slow cooling normally results in the formation of coarse crystals, the consistency of a fat might be expected to largely depend upon the extent to which it had been previously heated and softened The consistency of fats is in fact dependent to some extent upon their previous heat treatment, but not nearly to the extent which might be expected If a sample of newly solidified shortening is immediately placed in a constant temperature bath at 70°F it will become somewhat harder than a similar sample tempered at 85°F for 24 hours and then brought to a temperature of 70°F If the sample is once so tempered, however, it may subsequently fluctuate widely in temperature (e g , between 40° and 90°F) and yet always revert to substantially the same consistency at 70°F

The ability of fats to thus retain their original crystal form through fluctuations in temperature is somewhat puzzling and cannot be fully explained on the basis of present knowledge of the subject Apparently the melting or dissolving fat crystals are capable of leaving behind invisible nuclei which serve as starting points for the development of new crystals when the fat is again cooled The phenomenon appears to be in some way related to the initial size of the crystals Lard and hydrogenated lard, which have characteristically large crystals, are more affected by variations in temperature and consequently more unpredictable in body, than hydrogenated vegetable oil shortenings or shortenings compounded from vegetable oil and tallow or oleostearine The difference in this respect between lard and vegetable oil products will be considered more fully on page 229

(i) *Thixotropy in Plastic Fats*

Fats exhibit the phenomenon of thixotropy to a considerable degree, i e , they become relatively soft when mixed or otherwise worked, and after working has ceased slowly regain their original consistency The thixotropic behavior of fats is presumably traceable to the breaking of cohesive and mutually attractive forces between the crystal particles in the agitated fat and the reestablishment of these forces after the fat has again come to rest So far as the author is aware, however, no study has been made of this phenomenon in its specific relation to plasticity in fats or fatty products

4 Lard and Other Animal Fats

(a) *Lard Production in the United States*

Approximately two thirds of the lard produced in the United States is manufactured in large meat packing establishments under Federal Government inspection The remainder is manufactured on farms or in small

establishments which do not ship lard outside the boundaries of their own states and consequently do not have their products federally inspected In 1940, the distribution of hogs slaughtered in the United States was estimated to be as follows.[8]

Wholesale establishments, federally inspected	50,398,000
Wholesale establishments, not federally inspected	8,857,000
Retail establishments	4,144 000
Farms	13,888,000
TOTAL	77,287,000

The U S production of lard in 1940 was 1,527,000,000 pounds from federally inspected establishments, and 769,000,000 pounds from all other sources, or an average amount of lard per hog slaughtered of 30 3 and 28 6 pounds, respectively

The raising of hogs is concentrated largely in the middle western states The production of hogs for slaughter in the leading producing states in 1939 was as follows [9]

Iowa	11,392,000
Illinois	6,046,000
Indiana	4,881 000
Minnesota	4,563 000
Ohio	4,048,000
Missouri	4,040 000
Nebraska	3,119,000
Wisconsin	2,703,000

Data relative to the production of lard in countries other than the United States will be found on page 105

(b) Different Varieties of Lard

Most of the lard produced in the United States is wet rendered in closed tanks under steam pressure Lard of standard quality produced by this method of rendering is designated as prime steam lard

The so called refined lard of commerce, which is marketed in tierces, drums, cans, tubs, pails, and cartons, is not refined in the sense that vege table oils are refined, since it receives no treatment with caustic soda or other alkali Refined lard consists simply of prime steam lard which has been dried, clarified (possibly with some degree of bleaching), and solidi fied Unless cartons and other packages of lard are given some specific designation, such as "kettle-rendered lard," "leaf lard," etc , their contents may be considered to be ordinary prime steam lard Such lard is often

[8] U S Bur Census, *Animal and Vegetable Fats and Oils*, 1938–1942 Washington, 1943

[9] U S Dept Agr , *Agricultural Statistics* Washington, 1943 and previous years

stiffened, however, by the addition of leaf lard, hydrogenated lard stearine, or lard stearine obtained as a residue in the manufacture of edible lard oil

In some plants ordinary lard is produced by a dry rendering process, rather than steam rendering Such lard cannot be labeled as prime steam lard, although it is sold and used for the same purposes Dry-rendered lard has a "cooked" flavor, somewhat different from that of prime steam lard, and is usually somewhat darker in color because it contains traces of colloidally dispersed protein materials Otherwise it is identical with the more common prime steam lard The flavor of dry-rendered lard is preferred by some users

Leaf lard refers specifically to lard rendered from the internal "leaf fat" of the animal Leaf lard is on the average perhaps 10 units lower in iodine value than ordinary prime steam lard from the same animal, and correspondingly firmer Leaf lard is almost always rendered by a dry process

TABLE 92

ANALYSES OF REPRESENTATIVE SAMPLES OF PRIME STEAM LARD, DRY RENDERED LARD, AND LEAF LARD

Analysis	Prime steam lard	Dry rendered lard	Leaf lard
	68 2	68 5	58 5
	0 30	0 25	0 15
	10Y-1 0R	15Y-1 8R	10Y-1 2R
	8 0	8 5	16 0
Titer, °C	38 2	37 5	41 5
Micropenetration, mm /10, at			
50°F	52	55	28
70°F	110	120	58
80°F	155	180	75
90°F	275	325	210
95°F	[a]	[a]	360

[a] Too soft to determine

in an open kettle The method of rendering gives the product a distinctive flavor In addition to being firmer than ordinary lard, leaf lard also has somewhat better keeping qualities It is in chief demand as a fat for household use, and it ordinarily sells at a slight premium over ordinary lard A limited amount of kettle rendered lard is produced from fatty tissues other than leaf fat

Neutral lard is a special product made by wet rendering selected stock at a low temperature, with the object of producing a very mild flavored fat for margarine manufacture Since the development of efficient processes for deodorizing vegetable oils, the production of this variety of lard has greatly declined

(c) *Variations in the Composition of Lard*

The composition and resulting characteristics of lard are subject to very wide variation They are affected by the feed of the hog, and are different in lard rendered from different parts of the carcass of the same animal

The hog has, to a high degree, the ability to assimilate ingested fat with little change in its component fatty acids Most of the vegetable oils which occur in the feed of the hog are more highly unsaturated than the fat synthesized by the animal from proteins or carbohydrates Consequently, the degree of unsaturation of hog fat depends to a great extent upon the amount of oil in the feed of the animal and its fatty acid composition

An extensive investigation of the factors influencing the composition of lard has been carried out by Ellis and co workers These investigators were chiefly concerned with the consistency of hog fat in its relation to the production of soft or "oily" bacon and other meat products

It was found by Ellis and Hankins[10] that there was a progressive decrease in unsaturation in the fat of corn fed hogs during the growth of the animal Certain data of these workers relative to hogs of different ages fed on a

TABLE 93

VARIATIONS IN THE FAT OF HOGS DURING THE GROWTH OF THE ANIMALS COMPOSITION AND CHARACTERISTICS OF THE COMPOSITE BODY FAT OF HOGS RAISED ON A DIET OF SKIM MILK AND CORN[a]

Approximate age of animals	Approximate weight of animals, lbs	Titer of fat °C.	I V of fat	Composition of fatty acids %		
				Sat d	Oleic	Linoleic
6 weeks	—	37 0	72 5	33 2	54 5	12 3
10-12 weeks	—	37 5	71 0	31 4	54 8	13 8
5 months	70	37 8	66 1	36 9	51 4	11 7
6 months	100	37 9	63 2	37 3	53 9	8 8
7 months	170	39 2	59 7	38 4	54 3	7 3
8 months	225	39 1	58 8	38 6	54 4	7 0

[a] From the data of N. R Ellis and O G Hankins, *J Biol Chem*, 66, 101 122 (1925)

diet of skim milk and corn are recapitulated in Table 93 The change in the fat of the hogs during the period of growth was ascribed to the observed fact that the rate of fat deposition steadily increased during this period This would lead to a progressively larger proportion of the fat being synthesized from carbohydrates rather than being derived from ingested oil in the corn fed to the animals In this and succeeding studies the actual consistency of the fat was observed to be closely related to its iodine value

Ellis and Isbell[11] examined the fat of hogs fed on a wide variety of diets Some of the results of their experiments are summarized in Table 94 It is noteworthy that the ingestion of different oils leads to distinctive arrangements in the proportions of the lard fatty acids Thus, the difference between the lard derived from corn fed hogs and hogs fed on brewer's rice and tankage is in the relative proportions of oleic and linoleic acids, the

[10] N R Ellis and O G Hankins *J Biol Chem*, 66, 101-122 (1925)

[11] N R Ellis and H S Isbell, *J Biol Chem*, 69, 219-248 (1926)

contents of saturated acids are substantially the same The feeding of either peanuts or soybeans produces a very soft lard, but the proportions of the fatty acids are very different in the two cases A trace of linolenic acid was detected in the fat of the soybean fed hogs

It was found by Ellis and Zeller[12] *that hogs could be raised to a good* weight and condition on a high protein diet almost completely devoid of fat Lard derived from such hogs was extremely firm and contained but a fraction of one percent of linoleic acid However, this lard, like that examined in preceding studies, contained traces of arachidonic acid

European lard is ordinarily somewhat lower in iodine value and firmer than American lard, due to the widespread use in European countries of skim milk and other feeds of high protein and low fat content Much of the lard produced in Europe has an iodine value below 60, whereas American prime steam lard from hogs fed on the usual diet of corn with a supple-

TABLE 94

EFFECT OF DIET ON THE FAT OF HOGS COMPOSITION AND CHARACTERISTICS OF THE COMPOSITE BODY FAT OF HOGS RAISED ON DIFFERENT FEEDS[a]

Feed	Brewer s rice with tankage	Corn with tankage	Peanuts (grazed)	Soybeans (grazed)
Oil content of feed,%	0 8	4 3	33 1	17 5
Iodine value of oil	100	126	93	128
Analysis of fat				
Iodine value	54 7	60 8	89 6	93 2
Refractive index at 40°C	1 4585	1 4590	1 4625	1 4630
Melting point, °C	37 3	39 1	19 4	26 0
Titer, °C	40 0	40 3	28 1	33 9
Saturated acids, %	39 3	39 3	20 6	27 2
Oleic acid %	58 7	52 1	58 0	32 0
Linoleic acid, %	2 0	8 6	21 4	32 0

[a] From the data of N R Ellis and H S Isbell *J Biol Chem*, 69, 219 248 (1926)

ment of tankage will have an iodine value which is seldom below 65 and often above 70

Soybeans are seldom fed to hogs in any quantity, but it is common practice in certain sections of the southern United States to fatten hogs by grazing them in fields of peanuts The extremely soft fat from such animals must be stiffened by the addition of considerable percentages of lard stearine before it can be packaged in cartons or used as a plastic fat It is not uncommon for prime steam lard from peanut fed animals to have an iodine value of 90 or higher

A rather pronounced seasonal variation has been observed by the author *in the lard from hogs received at a middle-western packing house* (see Fig 14) The iodine value is at a maximum in the summer and at a minimum in the late fall, with a spread of approximately 5 units between the

[12] N R Ellis and J H Zeller, *J Biol Chem*, 89, 185–197 (1930)

average values for the high and low months. This variation in iodine value is accompanied by a parallel variation in the consistency of the lard, but there appears to be little or no correlation between iodine values and the stability of the fat.

The iodine value of fat from a single animal is progressively higher from the internal organs outward toward the skin. Thus the leaf fat of a hog produces lard with the lowest iodine value, and the back fat produces lard with the highest iodine value. Since the same proportional amount of fat is usually taken from all parts of the carcass for the manufacture of prime steam lard, this circumstance does not result in any great degree of variation in the iodine value in ordinary packing house practice. However, changes from time to time in the methods of cutting the carcass and trimming the cuts may affect the characteristics of the lard to some degree. The weight and degree of fatness of the animal have something to do with

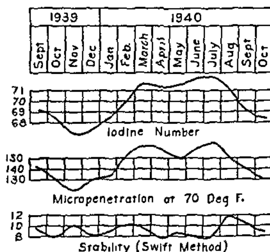


FIG. 14.—Seasonal variations in the characteristics of cutting lard

the character of the lard. Heavy and fat hogs have a higher ratio of outer to internal fat than lighter and less fat animals.

(d) Consistency of Lard

The factors influencing the iodine value of lard otherwise affect its consistency, as these two properties are related. Differences in the unsaturation of lard amounting to two or three iodine units are not always reflected in the consistency of the product, but in general the firmness of lard is in inverse proportion to its iodine value.

In the large packing houses, it is common practice to produce two varieties of prime steam lard, namely "killing lard" and "cutting lard." The killing lard is obtained from fatty stock which is removed from the carcass at the time the animal is killed. Since a large portion of the killing fat is trimmed from the internal organs of the animal, the lard from this fat is

relatively firm and low in iodine value The cutting lard is rendered from stock obtained from the cutting floor, where the chilled carcass is divided into the various pork cuts As this stock largely consists of fat trimmed from beneath the skin, cutting lard is softer and higher in iodine value than killing lard

The usual ratio of killing to cutting lard produced is about 35 to 65 Prime steam lard usually consists of a mixture of these two varieties of lard in approximately these proportions

Variations in the consistency of different samples of lard are illustrated by the micropenetration curves of Figure 15 These curves represent a variety of lards, ranging from a very soft cutting lard to a normal leaf lard All of the lards of this series were rendered from corn fed animals Peanut fed, or other "oily" hogs, produce lard considerably softer than the

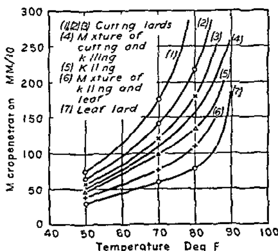


Fig 15 —Micropenetrations of typical samples of lard

softest lard of the series Most European lard would approach the consistency of the leaf lard Leaf lard from corn fed hogs is, incidentally, quite uniform in consistency and appears to be less subject to variation than the outer fat of the animals

Adjustment of Lard Consistency—Since the consistency of ordinary American prime steam lard is rather softer than is desirable, particularly when the product is destined for export to Europe, it has become common practice to stiffen prime steam lard by the addition of a small proportion of hydrogenated lard stearine The stearine is prepared by deodorizing lard which has been refined and then hydrogenated to a low iodine value It usually has a titer between 55° and 60°C , and is added in amounts ranging between about 5% and 10%

For purposes of control it is convenient to combine the micropenetrations at 50°, 70°, and 80°F into a single figure which gives approximately

equal weight to the consistency at each temperature Such a figure is the "consistency index," which is defined as follows

where a, b, and c are the micropenetrations in tenths of millimeters at 50°, 70°, and 80°F, respectively,

$$\text{consistency index} = (7a + 3b + 2c)/10$$

Leaf lard usually has a consistency index quite close to 50 The index of killing lard is usually between 75 and 100, whereas that of cutting lard is usually between 110 and 150 However, it may be 160 or 170, or in exceptional cases even higher

As hydrogenated lard stearine is somewhat variable in its hardness and consequent stiffening properties, and as lards of different consistencies require different degrees of stiffening, selection of the proper amount of stearine to be added is often a matter of some difficulty

The charts of Figures 16 and 17 have been found useful as a guide to the amount of hydrogenated lard stearine to be added for converting lard from one consistency index to another The curves of Figure 16 represent 15 arbitrarily selected "degrees of stiffening" The curves of Figure 17 represent the same 15 degrees of stiffening, in terms of percentages of lard stearine of various titers A single example will suffice to show the manner in which the charts are used Suppose, for example, that it is desired to stiffen lard with a consistency index of 140 to a consistency index of 70, by the addition of 52° titer stearine Reference to Figure 16 will reveal that the desired change in consistency involves 8th degree stiffening From Figure 17 it may be seen that stiffening of the 8th degree will be obtained by mixing approximately 9% of 52° titer stearine with 91% of the soft lard

If it is desired to effect a comparable stiffening by adding leaf lard rather than lard stearine, Figure 18 may be similarly used as a guide

The titer of a lard is a quite reliable indication of its consistency, provided that it contains no hydrogenated lard Hydrogenation of lard, or the addition of lard stearine to lard, stiffens the product to a greater degree than is indicated by the change in the titer The average relationship between the titer and the consistency of lards is shown graphically in Figure 19

(e) *Stability of Lard*

Lard is much less stable than equally unsaturated hydrogenated vegetable oil shortenings In accelerated oxidation tests by the Swift method, even the more stable lards with iodine values of 62 or 63, will seldom keep longer than about 10 to 12 hours Hydrogenated cottonseed, soybean, or peanut oils of the same iodine value will keep 75 to 150 hours

The limited resistance of lard to oxidation appears to be due to its almost complete lack of natural antioxidants Hydrogenated vegetable oils which

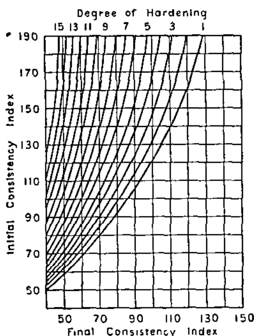


FIG 16 —Chart I for adjustment of the consistency of lard change in consistency index corresponding to various degrees of hardening

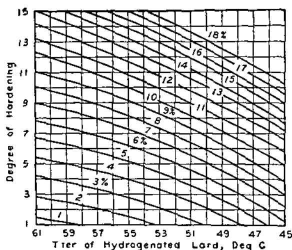


FIG 17 —Chart II for adjustment of the consistency of lard amount of hydrogenated lard stearine to be incorporated to attain various degrees of hardening

have been deprived of the bulk of their antioxidants by molecular distillation[13] behave very similarly to lard when subjected to accelerated oxidation tests Some progress has been made in recent years in improving the

[13] A E Bailey, G D Oliver, W S Singleton, and G S Fisher, *Oil & Soap*, 20, 251-255 (1943).

stability of lard by more careful processing However, a very limited stability, in comparison with vegetable shortenings, is inherent in the product, in its pure state

Various antioxidants from other edible plant and animal materials have been proposed for addition to lard to improve its keeping qualities These

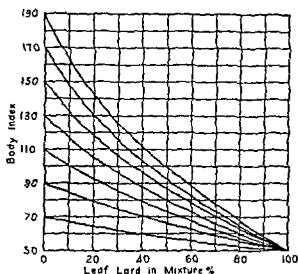


Fig 18 —Chart III for adjustment of the consistency of lard amount of leaf lard to be incorporated to produce different changes in the body or consistency index

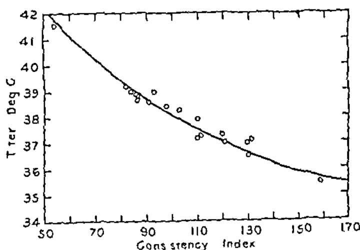


Fig 19 —Titer *vs* consistency index of lard

include tocopherols and also phosphatides from corn oil,[14] cottonseed oil,[14] soybean oil,[15] and the brain tissues and other tissues of animals [16]

Actually, phosphatides from any source are of little benefit in ordinary

[14] B H Thurman (to Refining, Inc), U S Pat 2,201,063 (1940)
[15] H Bollman, U S Pat 1,464,557 (1923)
[16] W F Douglass (to Cudahy Packing Co), U S Pat 2,071,457 (1937)

In the absence of tocopherols or other antioxidants of the phenolic , phosphatides improve the stability of lard but little They tend to e the fat to foam, and also are inclined to produce a fishy odor in the ifter the latter has become slightly oxidized Due to their foam ucing tendencies, phosphatides are not usually added to any fat in ter amounts than a small fraction of one per cent

itents have been issued covering the addition of minor amounts of ous vegetable oils to lard These vegetable oils include palm oil,[17] ogenated sesame oil,[18] crude cottonseed oil,[19] crude soybean oil,[20] ogenated soybean oil,[21] and kapok oil [22] The steam distillate resulting the deodorization of sesame oil has also been patented [23]

general, the vegetable oils may be said to be somewhat more effective romoting the stability of lard than phosphatides From 5% to 10% ne of the above oils will usually more than double the accelerated keep- time of lard or hydrogenated lard However, a fat containing this ortion of a vegetable oil is actually a compound, rather than a true , and cannot be labeled and sold as lard

atents[24] have been issued on oat flour and a great variety of other solid table substances for incorporation into lard to improve its stability vever, there are obvious disadvantages in the use of any solid material this purpose

he one antioxidant which has been satisfactory enough on all counts to ive extensive commercial use is not derived from food materials, al- igh it is a natural product This antioxidant is gum guaiac,[25–27] which btained from the tropical American tree, *Guaiacum officinalis* The ial active compounds in gum guaiac have not been fully determined, they appear to be phenolic in type The keeping time of lard treated 1 0 05% of gum guaiac is extended to several times its original value his concentration, the substance imparts no noticeable flavor or odor he lard A significant property of gum guaiac is its ability to afford

R C Newton and W D Richardson, (to Swift & Co), U S Pat 1,890 585 3)

D P Grettie (to Swift and Co), Brit Pat 395 971 (1933)

D P Grettie and R C Newton (to Swift and Co), Brit Pat 415 205 (1934)

D P Grettie (to Industrial Patents Corp), U S Pat 2 052 289 (1936)

D P Grettie (to Industrial Patents Corp), U S Pat 2 201,692 (1940)

V C Mehlenbacher (to Industrial Patents Corp) U S Pat 2 108,922 (1938)

D P Grettie (to Industrial Patents Corp), U S Pat 2 095 740 (1937)

S Musher (to Musher Foundation Inc) U S Pat 2 026 697 (1938), and sub ient patents See also F N Peters and S Musher *Ind Eng Chem* , 29, 146–151 7)

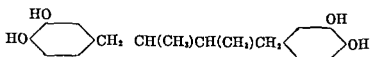
D P Grettie, *Oil & Soap*, 10, 126–127 (1933)

H S Mitchell and H C Black, *Ind Eng Chem* , 35, 50–52 (1943)

R C Newton and D P Grettie (to Swift & Co), U S Pat 1,903 126 (1933)

protection to the fat after the latter has been incorporated into crackers or other prepared foods It is completely lacking in toxicity [28]

Another substance of plant origin which has recently received much attention as a possible antioxidant for lard is nordihydroguaiaretic acid [29]



which occurs in the common desert plant, *Larrea divaricata*, or creosote bush This antioxidant extends the keeping time of the lard remarkably, in one test for example, lard keeping 11 hours initially by the Swift method had its keeping time extended to 210 hours by the addition of 0 01% nordihydroguaretic acid However, it is not stable in contact with alkaline substances, and thus it loses much of its effect when baked into soda crackers

Fat soluble fatty acid esters of *l* ascorbic and *d* isoascorbic acids have been recommended as acid type antioxidants for lard [30] These compounds are particularly effective when used in conjunction with added commercial lecithin and tocopherols

Synthetic antioxidants of the phenolic type have not as yet been used for stabilizing lard The compounds which are known to have strong antioxygenic properties are, almost without exception, too volatile, too strong in flavor and odor, too unstable, or too toxic to be suitable for use in edible products It seems not unlikely, however, that new compounds may eventually be developed which will not have these undesirable properties and which may be as satisfactory from all standpoints as the antioxidants occurring naturally in vegetable oils One shortcoming which is shared by most of the synthetic antioxidants is an unduly low molecular weight The vegetable oil antioxidants are usually sufficiently high in molecular weight to survive the drastic treatment of high temperature, high vacuum deodorization Compounds which retain the functional hydroxyl groups of such antioxidants as hydroquinone, pyrogallol, catechol, etc , but are weighted by the addition of long side chains or other heavy molecular fragments would probably have much of the effectiveness of the simpler antioxidants without some of their disadvantages In this connection, the decreasing toxicity of resorcinol with increasing length of a substituted side chain is of interest [31]

[28] V Johnson, J Carlson, N Kleitman, and P Bergstrom, *Food Research* 3, 555 574 (1938)

[29] W O Lundberg H O Halvorson, and G O Burr, *Oil & Soap*, 21, 33–35 (1944)

[30] R W Riemenschneider, J Turer, P A Wells, and W C Ault, *Oil & Soap*, 21, 47–50 (1944)

[31] See A R L Dohme, E H Cox, and E Miller, *J Am Chem Soc* , 48, 1688–1693 (1926)

Research in the field of synthetic antioxidants must however, necessarily be slow not only because of the complexity of the substances to be investigated but also because of the necessity for establishing their lack of toxicity beyond question before they can be accepted for edible use Antioxidants of the acidic type are relatively ineffective in lard because the action of these substances is only accessory to that of phenolic type antioxidants, which are not present in lard to any useful extent

(f) Rendered Pork Fat

Since 1940 regulations of the U S Department of Agriculture have provided that the fat rendered from certain low grade stocks shall not be labeled and sold as lard, but must be designated "rendered pork fat" The regulations of the Bureau of Animal Industry which define lard and rendered pork fat are as follows

Lard The fat rendered from fresh clean sound fatty tissues from hogs in good health at the time of slaughter with or without lard stearine or hardened lard The tissues do not include bones detached skin head fat ears tails organs windpipes large blood vessels scrap fat skimmings settlings pressings and the like and are reasonably free from muscle tissue and blood

Rendered pork fat The fat other than lard rendered from clean sound carcasses parts of carcasses or edible organs from hogs in good health at the time of slaughter except that stomachs tails bones from the head and bones from cured or cooked pork are not included The tissues rendered are usually fresh but may be cured cooked or otherwise prepared and may contain some meat food products Rendered pork fat may be hardened by the use of lard stearine and/or hardened lard and/or rendered pork fat stearine and/or hardened rendered pork fat

The production of rendered pork fat amounts usually to about 10% of the total amount of hog fat rendered in government inspected establishments Rendered pork fat has been included with lard in the statistics previously quoted on the production of lard

(g) Hydrogenated and Deodorized Lard Products

Since about 1929 one large American meat-packing company has marketed a neutral, hydrogenated lard shortening [32] In the manufacture of this product a cutting lard or other soft lard is first refined with sodium bicarbonate or caustic soda, to reduce its content of free fatty acids to 0 02% or 0 03% The refined lard is filtered and is then hydrogenated under conditions similar to those employed in the manufacture of an all hydrogenated vegetable shortening, until a desirable consistency is obtained The degree to which the product may be hydrogenated depends to some extent upon the original iodine value of the lard, if a lard with an iodine value as high as 71 is available, its iodine value may be reduced by

[32] J R Shipner (to Cudahy Packing Co) U S Pat 1 755 135 (1930)

bout 9 units, to yield a finished product with an iodine value of about 62 f the iodine value of the lard is as low as 66, it may not be possible to reduce t more than about 6 units, in which case the iodine value of the product will be about 60

After the hydrogenation, the product is deodorized, and is then solidified nd packed in the same manner as vegetable shortenings The product, fter hydrogenation, is somewhat easier to deodorize than vegetable oils r vegetable shortenings

Hydrogenated lard represents a considerable improvement over ordinary ard in many respects The characteristic flavor and odor of lard is per manently removed A considerable increase in stability is conferred upon he product, its average keeping time, by the Swift method, is about 25 ours, as compared with about 8 to 10 for plain lard It has a more desir

TABLE 95

CHARACTERISTICS OF REPRESENTATIVE SAMPLES OF NEUTRAL LARD PRODUCTS *IN COMPARISON WITH ORDINARY PRIME STEAM LARD*

Analysis	Lard shortening all hydrogenated type	Lard shortening blended type	Prime steam lard
Iodine value	61 0	64 0	68 2
Free fatty acids % as oleic	0 03	0 03	0 30
Smoke point, °F	*440*	*440*	*360*
[illegible]	5Y-0 1R	5Y-0 8R	10Y 1 0R
[illegible]	25	25	9
[illegible]			
[illegible]	18	20	52
70°F	45	50	110
80°F	78	80	155
90°F	160	120	275
95°F	260	145	[a]

[a] Too soft to determine

ble consistency than unhydrogenated lard, and it can also be made more niform in consistency Hydrogenation also whitens the lard, improves s appearance, and improves its baking qualities

Another large meat packer also manufactures a neutral lard shortening his product, which has been on the market since about 1939, is prepared y refining lard, stiffening the refined lard by blending with it a suitable roportion of hydrogenated lard stearine, and deodorizing the mixture he product is stabilized by the addition of gum guaiac [26] *This second,* lended product, when so stabilized, possess most of the advantages of the rst, all hydrogenated type, as mentioned above, and is somewhat more niform in consistency and stability

Although the neutral lard products represent a considerable improve ent over *ordinary raw* lard, *in the present* state of their development hey are deficient in some respects in comparison with vegetable oil shorten

ings Due possibly to its containing traces of arachidonic or other highly unsaturated acids, lard is not equivalent in stability to high grade vegetable oil shortenings even when fortified with antioxidants from foreign sources This is particularly true with respect to its resistance to flavor reversion Hydrogenated lard is susceptible to a peculiar type of flavor reversion When packed in cartons or other containers which give it more or less free access to the air, it remains relatively flavorless; but, if sealed in cans with a limited supply of oxygen, it develops a slight tallowy or muttony odor

Experiments have proved that the merest traces of oxygen will produce this flavor reversion In order to avoid it, the fat must be completely protected from access to air from the time it is removed from the deodorizer until the can is sealed Also an oxygen free gas must be used, both for incorporation into the fat and for filling the head space of the can As commercial nitrogen is insufficiently free from oxygen for this purpose, it is at present impracticable to pack hydrogenated lard in sealed cans or jars

Both types of neutral lard are somewhat different in texture from vegetable oil products, because of their relatively coarse crystal structure

One of the characteristics of lard which has been undesirable in the past is its highly unpredictable consistency or body Part of the lack of uniformity of lard in this respect is due to variations in the actual composition of the fat However, some variability in the body of lard can be traced to the failure of this fat to respond uniformly to changes in its temperature This latter cause of nonuniformity cannot be eliminated by hydrogenation of the lard or adjustment of its body by means of added lard stearine

Lard products are rather different from vegetable oil shortenings in this respect If a vegetable oil is brought to a definite consistency, either by hydrogenation or by the addition of a hard fat, and then properly solidified and tempered, its body thereafter will at any temperature be both definite and predictable Under the same conditions the body of a lard product will vary considerably

The difference between lard and other fats is well illustrated by the relationships prevailing between the micro and macropenetrations of hydrogenated lard and hydrogenated cottonseed oil (see Figs 20 and 21) In the determination of micropenetrations the fat is solidified in the laboratory under carefully controlled and standardized conditions, so that variations in the penetrations are caused only by differences in the composition of the fat Macropenetrations, however, are determined upon the commercially solidified samples, so that variations in the consistency of the fat may be introduced by the heat treatment of the sample prior to its examination, if the fat is susceptible to such influences It will be seen, for example (Figs 20 and 21), that hydrogenated cottonseed oil with a micropenetration of 65 can be expected to have a consistency after it is commercially solidified corresponding to a macropenetration of between 49 and 53 Hydro-

genated lard with the same micropenetration may have a macropenetration anywhere between about 38 and 80

Lard is the only fat which exhibits this peculiar behavior The reason for it appears to be inherent in the structure of the lard glycerides, it is quite possibly related to the coarse crystal structure of the fat This characteristic of lard can only be eliminated by application of the rearrangement reaction (see pages 681–682), to break up completely the natural configuration of glycerides in the fat

(h) Plastic Oleo Oil

A small amount of oleo oil of both extra and prime grades is converted to a plastic product by solidification in equipment similar to that used for

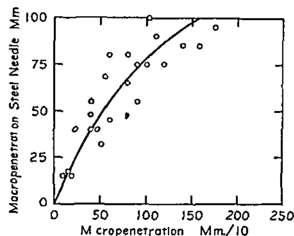


Fig 20 —Micropenetrations *vs* macropenetrations of hydrogenated lard

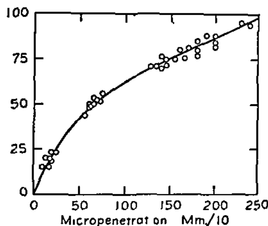


Fig 21 —Micropenetrations *vs* macropenetrations of hydrogenated cottonseed oil

lard and shortenings The solidified product is packed in drums and sold to the bakery and confectionery trade It is only suitable for certain specialty uses, and is not packaged for household consumption Oleo oil is not a good shortening for general use because of its very limited plastic range

Plastic oleo oils are often stabilized by the addition of approximately 0 1% of soybean lecithin Lecithin is a very effective antioxidant for oleo oil, even though this oil contains little or no tocopherols The addition of 0 1% will increase the stability of this product from 8 to 15 hours to about 60 hours, as measured by the Swift method The stabilizing effect of the lecithin is lost, however, after the fat is baked into crackers, cookies, etc

5 Shortenings

(a) Different Types

Shortenings, as manufactured in the United States, fall into two distinct classes, which are respectively those of the *compound* or *blended* type and

ose of the *all hydrogenated* type Compound type shortenings may be rther divided into *animal and vegetable* fat compounds and *all vegetable* mpounds All hydrogenated shortenings may be subdivided into *regular general purpose* shortenings, *biscuit and cracker type* shortenings, and *perglycerinated* shortenings

In the earlier days of shortening manufacture, there was a distinct differ ce in composition between products of the compounded and all hydro nated types Where hydrogenation was used in the preparation of com unds, the invariable practice was to highly hydrogenate a minimum oportion of oil and blend this with untreated oil Now it is common prac e to blend highly hydrogenated oil with slightly hydrogenated oil or even blend three or more fats or oils, all of which have been hydrogenated to fferent degrees Thus, insofar as the composition of the products is ncerned, the distinction between compounds and all hydrogenated short ings is no longer clear cut However, the two products continue to be fferentiated by other characteristics All hydrogenated shortenings are ore carefully and thoroughly refined and deodorized, and are of generally gher quality than compounds They sell at a price substantially above at of compound shortenings In some respects all hydrogenated short ings are superior to compounded shortenings principally because of the creased care customarily taken in their manufacture In several im ortant particulars, however all hydrogenated shortenings and shortenings f the true compound type are fundamentally different

All hydrogenated shortenings are naturally more stable than com- ounded or blended shortenings Most compounded shortenings contain om 80% to 90% of untreated highly unsaturated oil The addition of 0% to 20% of hard fat to the oil does not produce a mixture with either its nsaturation or stability greatly improved over that of the original oil lost compounds have an iodine value of about 90 and contain 40% or ore of linoleic acid The keeping quality, by the Swift method, of a ompound made with cottonseed oil, is about 16 to 18 hours, as compared ith about 12 to 16 hours for the original oil

In contrast to the compounds, an all hydrogenated cottonseed oil hortening will usually have an iodine value of 60 to 65 and a linoleic acid ontent not greater than 5% to 10% The Swift keeping time of such a hortening will be not less than 70 hours The disparity in keeping uality between the two types of shortening is accentuated by the custom ry practice of packing compounds for household use in cartons and other nsealed containers and packing similar all hydrogenated shortenings in air ight cans or jars

The second fundamental point of difference between the two types of hortening is in their plastic range and their change in consistency with ariations in temperature Compound type shortenings naturally have

a longer plastic range than all-hydrogenated shortenings, and are both softer at low temperatures and firmer at high temperatures. The difference in this respect between representative samples of the two types is shown graphically in Figure 22.

The range of macropenetrations within which a shortening is at the best consistency for working and mixing is about 40 to 90 mm. It will be seen that a typical compounded shortening is within this range of penetrations between about 45° and 104°F A typical all-hydrogenated shortening will have the same consistency only within the more restricted range of about 64° to 87°F.

Biscuit- and cracker-type shortenings and superglycerinated shortenings are modified forms of the regular all-hydrogenated type. They have been developed to meet the specialized requirements of commercial bakers for products with high stability and strong emulsifying properties, respectively.

(b) Production and Consumption

The production of shortenings in the United States has varied between about 1 0 and 1.5 billion pounds in recent years. This corresponds to a per capita consumption of 7 5 to 12 5 pounds per year. The consumption of shortening tends to be related to that of lard, being lowest when much lard is consumed and highest when the production of lard is restricted (see Table 96).

Complete statistics are not available on the relative volumes in which the various types of shortening are manufactured. However, the following indirect figures (in pounds) for the year 1940[32a, 33] are of interest:

Total factory production of shortening	1,190,000,000
Factory production of hydrogenated oils	803,000,000
Compounds containing animal fat, prepared under federal inspection	203,000,000
Naturally liquid oils used in the manufacture of margarine	205,000,000

The factory production of hydrogenated oils includes all-hydrogenated shortening, hydrogenated oil used in the production of compounds, most of the naturally liquid oils used in margarine, and a small tonnage of inedible products Considering all factors, it appears probable that the production of the various types of shortening during this year was approximately as follows (in pounds):

Animal and vegetable compounds	200,000,000
All vegetable compounds	500,000,000
All-hydrogenated shortening	500,000,000
TOTAL	1,200,000,000

[32a] U. S Bur. Census, *Animal and Vegetable Fats and Oils*, 1938–1942 Washington, 1943

[33] U S Dept Agr , *Agricultural Statistics* Washington, 1943 and previous years

There is a considerable use of shortenings in Canada, Mexico, and other countries of Central and South America The only countries outside the Western Hemisphere which consume much shortening are the United Kingdom and Russia The United Kingdom reported a production of 240,000,000 pounds in 1937 [33a] No statistics are available on the Russian production in recent years

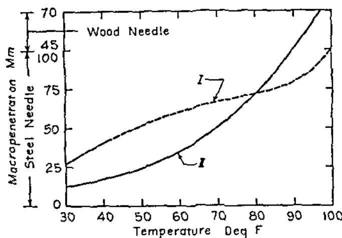


FIG 22 —Macropenetration curves of typical samples of all hydrogenated (II) and blended (I) shortenings

TABLE 96

PER CAPITA CONSUMPTION IN POUNDS OF LARD AND SHORTENING IN DIFFERENT YEARS IN THE U S [a]

Year	Lard	Shortening	Both fats
1930	12 7	9 8	22 5
1931	13 5	9 4	22 9
1932	14 3	7 5	21 8
1933	13 9	7 6	21 5
1934	12 8	9 5	22 3
1935	9 6	12 1	21 7
1936	11 3	12 4	23 7
1937	10 4	12 4	22 8
1938	10 9	11 6	22 5
1939	12 4	10 7	22 1
1940	14 7	9 0	23.7

[a] U S Dept Agr , *Agricultural Statistics*

(c) *Raw Materials for Shortening Manufacture*

Since a suitable consistency in shortening may be obtained both by blending hard and soft fats and hydrogenating soft fats, a very wide variety of oils may be used in the manufacture of this product

[33a] Imperial Economic Committee, *Vegetable Oils and Oilseeds* H M Stationery Office London, 1938

a longer plastic range than all-hydrogenated shortenings, and are both softer at low temperatures and firmer at high temperatures. The difference in this respect between representative samples of the two types is shown graphically in Figure 22

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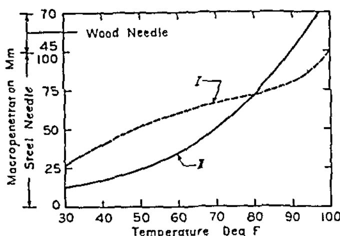


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1935	9 6	12 1	21 7
1936	11 3	12 4	23 7
1937	10 4	12 4	22 8
1938	10 9	11 6	22 5
1939	12 4	10 7	22 1
1940	14 7	9 0	23 7

[a] U S Dept Agr , *Agricultural Statistics*

(c) *Raw Materials for Shortening Manufacture*

Since a suitable consistency in shortening may be obtained both by blending hard and soft fats and hydrogenating soft fats, a very wide variety of oils may be used in the manufacture of this product

[15a] Imperial Economic Committee, *Vegetable Oils and Oilseeds* H M Stationery Office London, 1938

Oleostearine and edible tallow are the two natural hard fats most widely used in shortening manufacture The proper percentages of these fats for stiffening a liquid oil are about 20% and 50%, respectively It is common, however, to use somewhat less tallow (25% to 40%) and obtain an additional stiffening effect by hydrogenation, or the addition of hydrogenated vegetable stearine Much rendered pork fat goes into shortenings, and sometimes lard is used as an ingredient when its price is less than that of the vegetable oils

Cottonseed oil, peanut oil, sunflowerseed oil, corn oil, and sesame oil are suitable ingredients for compounded shortenings without being hydrogenated Soybean, fish, and whale oils are customarily hydrogenated considerably before being incorporated into shortenings in order to minimize their tendency to flavor reversion Fish oil is used only in the cheaper grades of shortening

High grade all hydrogenated shortenings are made principally from cottonseed, soybean and peanut oils Cottonseed and peanut oils may be used freely and interchangeably, but more than about 25% of soybean oil is not usually used in this type of shortening because of its flavor reversion and its disagreeable odor at frying temperatures Fish oil, whale oil, rapeseed oil, or other oils containing highly unsaturated acids are used very sparingly, or not at all Palm oil is a suitable ingredient for either type of shortening, but is usually subjected to some degree of hydrogenation, because of its dark color and the pronounced bleaching effect of this process

Coconut oil and other lauric acid oils are not among the more desirable materials for shortening manufacture, because of their short plastic range and their tendency to foam when used for deep frying They are used in minor amounts in many shortenings, but only relatively low grade products contain large proportions of these oils

The fats and oils used in the manufacture of all classes of shortenings in the United States in recent years are listed in Table 97 In the United Kingdom, cottonseed oil, whale oil, and peanut oil comprise the principal materials used in shortenings, very little shortening containing animal fats is manufactured The principal shortening oils in Russia are sunflowerseed, cottonseed, and linseed oil

(d) *Animal and Vegetable Compounds*

In the United States, there is a rather sharp distinction between compounds containing both animal and vegetable fats and those made exclusively from vegetable oils, because of the necessity of the former's being made under Federal Government inspection Practically all of the animal and vegetable compounds are manufactured by meat packing companies Although compounds of this class originally constituted the whole of the

United States' shortening production, they have been decreasing in importance for a number of years, and are now much exceeded in volume by the vegetable shortenings

Somewhat less than one half the animal and vegetable shortening produced at present is made to the original formula of approximately 20% oleostearine and 80% cottonseed oil (or other vegetable oil) The remainder is largely made from vegetable oil and tallow, with an average tallow content in the neighborhood of perhaps 35% Most of the shortening containing tallow is either stiffened by slight hydrogenation, or stiffened

TABLE 97

OILS AND FATS CONSUMED IN MILLION POUNDS IN THE MANUFACTURE OF SHORTENINGS IN THE U S IN RECENT YEARS[a]

Oil or fat	1937	1938	1939	1940	1941	1942
Cottonseed oil	1 163	1 051	905	823	889	694
Soybean oil	91	137	202	212	216	336
Palm oil	124	115	113	33	86	29
Peanut oil	58	52	52	23	82	38
Coconut oil	13	26	21	18	22	5
Corn oil	2	0	1	1	0	4
Rapeseed oil	5	0	0	0	0	0
Sesame oil	29	5	1	0	0	0
Babassu oil	0	1	1	0	0	0
Linseed oil	2	0	0	0	0	0
Oleostearine	30	33	26	17	23	31
Edible tallow	66	74	57	40	41	56
Lard and rendered pork fat	1	3	7	17	51	62
Fish oils	21	17	20	11	6	6
Other oils	1	1	1	1	1	26
TOTAL	1 605	1 517	1 406	1 196	1 418	1 287

[a] U S Bur Census *Animal and Vegetable Fats and Oils* 1938 1942 Washington 1943

by the addition of a small proportion (*e g*, 5%) of hydrogenated vegetable stearine

Slight hydrogenation of a mixture of 20% oleostearine and 80% cottonseed oil has the peculiar effect of softening the mixture in the range of about 90° to 100°F rather than stiffening it, as might be expected The following is a typical series of variations in the 98°F macropenetrations of such a mixture hydrogenated to different degrees

Unhydrogenated mixture	42 mm (wood needle)
Iodine value reduced 4 units	48 mm
Iodine value reduced 6 units	52 mm
Iodine value reduced 8 units	58 mm
Iodine value reduced 14 units	52 mm

A similar effect is noted in hydrogenating a mixture of hydrogenated vegetable stearine (iodine value 10–15) and cottonseed oil However, the addition of a small amount of stearine to vegetable oil which is to be made into all hydrogenated vegetable shortening will improve the 98°F body of the product, and 3% to 5% is often used for this purpose

If much tallow is to be used in a blended shortening formula, with or without slight hydrogenation, it is impossible to maintain the proportion of tallow constant and at the same time turn out a product of uniform consistency This is because there are considerable variations in the hardness of different lots of commercial edible tallow In Table 98 are some micropenetrations of different shipments of edible tallow, from various sources

TABLE 98
VARIATIONS IN THE HARDNESS AND UNSATURATION OF EDIBLE TALLOW FROM A VARIETY OF SOURCES

Sample No	Source	Iodine value	Micropenetrations mm /10 at 70°F
1	U S , Omaha, Nebraska	47	31
2	U S , Omaha, Nebraska	42	23
3	U S , St Paul, Minnesota	40	20
4	U S , St Paul Minnesota	40	21
5	U S , Sioux City, Iowa	43	27
6	U S , Sioux City, Iowa	41	23
7	U S , Atlanta, Georgia	37	17
8	U S , Camden, New Jersey	51	41
9	Argentina	42	21
10	Argentina	49	38
11	Uruguay	47	31
12	Paraguay	48	30
13	Paraguay	44	27
14	New Zealand	42	25
15	Australia	40	21
16	Australia	41	24

Since tallow has become an important ingredient of animal and vegetable shortenings, and cottonseed oil has been supplemented by large supplies of soybean and other vegetable oils, the blending of compound shortenings has become a somewhat involved matter Obviously, an almost infinite variety of blends are possible The analyses recorded in Table 99 will give some idea of the characteristics of certain shortenings of representative formulas

Animal and vegetable compounds are packed in all the standard shortening packages Probably a greater proportion of the total production goes into household packages than is the case with either all vegetable compounds or all hydrogenated shortenings

(e) *All Vegetable Compounds*

All vegetable compounds are similar in composition to animal and vegetable compounds, with the exception that highly hydrogenated vege

table oils are substituted for the hard animal fats which are used in the latter class of products

If an all vegetable shortening is to be made with a minimum amount of hardened oil the latter is usually hydrogenated to an iodine value of 15 or less In the case of a shortening which is to be made entirely of cottonseed oil, about 10% to 15% of hardened oil or vegetable stearine is required in the mixture, the exact amount depending upon the iodine value and titer of the stearine If the vegetable stearine is prepared from an oil containing a larger proportion of C_{18} acids than cottonseed oil, as for example, soybean oil, slightly less may be required, since such an oil will produce stearine with a relatively high titer If it is prepared from an oil containing less C_{18} acids such as palm oil, slightly more may be needed The consistency of such a compound is quite similar at all temperatures to that of an animal and vegetable compound containing oleostearine

TABLE 99

ANALYSES OF REPRESENTATIVE SAMPLES OF ANIMAL AND VEGETABLE COMPOUNDS

Analysis	20% oleostearine 80% cotton oil	55% tallow 45% cotton oil	5% hydrogenated stearine[a] 45% tallow 50% cotton oil	5% vegetable stearine[b] 35% tallow 60% cotton oil
Extent hydrogenated (decrease in iodine units)	0	0	2	6
Free fatty acids %	0 20	0 15	0 12	0 10
Iodine value	91 2	72 5	72	78
Color Lovibond scale	20Y 2 7R	20Y 2 6R	20Y 2 0R	20Y 2 2R
Stability Swift method hrs	12	14	18	20
Flavor and odor	Slight	Slight	Slight	Slight
Macropenetrations at				
50°F	40	30	28	31
70°F	60	55	50	53
80°F	68	70	60	61
90°F	75	90	73	79
95°F	82	50[c]	85	99

[a] Iodine value 11 titer 57 0°C
[b] Iodine value 12 titer 59 5°C
[c] Wood needle

If soybean oil or other oil which is inclined to revert in flavor is to be used in limited quantities in a compounded shortening it is usually desirable to hydrogenate this oil as much as is possible In such a case the more unstable oil may be hydrogenated to the approximate consistency of tallow and blended with cottonseed, peanut or other more stable oils in the same proportions in which tallow is used in animal and vegetable compounds A similar procedure is desirable when whale or fish oils are to be used in shortenings of this type Hydrogenation may, in fact, be considered very nearly as essential in the manufacture of blended shortenings as in all hydrogenated products of the all hydrogenated type It is possible, of course, for a manufacturer to produce a blended shortening without the

benefit of hydrogenation facilities, but in so doing he is severely limited in his choice of raw materials

Coconut oil, as stated previously, yields a shortening of rather poor plastic range If coconut oil is to be used in a shortening in large proportions, the product is best made by blending unhydrogenated coconut oil with about 8% to 12% of vegetable stearine and as much cottonseed oil or other liquid oil as may be permissible to use Completely hydrogenated coconut oil has a melting point of but 110°F, hence vegetable stearine cannot be made from this oil

Most of the all vegetable shortening manufactured in the United States is prepared from cottonseed, soybean, and peanut oils, although if available, corn, palm, sesame, or sunflower oils are entirely suitable materials

TABLE 100
ANALYSES OF REPRESENTATIVE SAMPLES OF ALL VEGETABLE COMPOUNDS

Analys s			5% vegetable o l	
Extent hydrogenated (decrease in iodine units)	0	6	6	60
Iodine value	97	92	76	72
Free fatty acids %	0 15	0 03	0 05	0 02
Color Lovibond scale	20Y 2 6R	20Y 2 8R	20Y-2 2R	15Y-1 8R
Keeping time hrs, Swift method	15	20	28	108
Flavor and odor	Slight	None	Slight	Slight
Macropenetration, mm, at				
50°F	48	44	32	25
70°	65	63	55	50
80°	74	73	68	65
90°	78	79	85	90
95°	82	84	96	55[a]

[a] *Wood needle*

When shortenings are made largely or entirely from soybean oils, they are usually prepared by hydrogenating the entire body of oil, even though they are to be marketed as compounds rather than as an all hydrogenated product Unhydrogenated soybean oil readily acquires a reverted flavor which is much more unpleasant than that of hydrogenated soybean oil, and the price of soybean oil is usually sufficiently below that of cottonseed oil to more than compensate for the slight added cost of hydrogenating the entire product

As indicated previously, the yearly production of all vegetable compounds in the United States is probably in the neighborhood of 500,000 000 pounds Usually, something over half of the total production of all vegetable compound is packaged and sold in small, household size containers The remainder is used by restaurants, hotels, doughnut fryers,

etc., and by commercial bakers whose class of trade does not justify the purchase of the more expensive all hydrogenated shortening

Some of the all vegetable compounds on the market are well refined and well deodorized, and when fresh are quite as satisfactory for many purposes as the all hydrogenated shortenings.

(f) All Hydrogenated Shortenings

The production of all hydrogenated shortenings in the United States has for some time been steadily increasing, both in actual volume and in relation to the total shortening manufactured At the present time probably one half the total shortening manufactured is of this type

All hydrogenated shortening is used to the near exclusion of all other fats by commercial bakers for making certain products, such as cakes and cookies It is also widely used in almost every other variety of baked product, and is popular with restaurants and hotels, and commercial deep fryers Considerable quantities are also consumed in home cooking, although the proportion so consumed is much less than that of the blended shortenings For commercial use, all hydrogenated shortening is packed in the usual drums and cans, but for household consumption it is put up in sealed 1- or 3 pound cans or jars

In the past, shortenings of this type have almost invariably been prepared either entirely from cottonseed oil or with cottonseed oil as a major ingredient The use of soybean oil has generally been limited to about 25% or less of the total oil Palm oil, sesame oil, sunflower oil, etc., have sometimes been used as minor ingredients

The preponderant use of cottonseed oil has been the result of relatively greater availability, rather than unique properties of the oil, there are several other oils which are equally good or perhaps superior raw materials for the purpose Peanut oil and soybean oil are both more stable than cottonseed oil when hydrogenated to the consistency of shortening, although at present the flavor reversion of soybean oil limits its use in high-grade products Sesame oil is particularly stable after hydrogenation, and is often used for its beneficial effect on the keeping quality of the product, whenever it is available Sunflower oil could be expected to be an entirely satisfactory material for all hydrogenated shortenings

Methods employed in the manufacture of all hydrogenated shortenings vary considerably Some manufacturers are accustomed to preparing two or more stocks of different iodine values and consistency, and blending these together to form the finished product This method has the advantage of eliminating the necessity for very carefully controlling the hydrogenation, as minor adjustments in the consistency of the product can be effected by varying the proportions in which the different stocks are blended However, by the proper techniques, the consistency of the fat

can be satisfactorily controlled during hydrogenation, otherwise there appears to be no advantage in the blending method Two different stocks mixed together to a given iodine value are never softer at ordinary room temperature than a single oil hydrogenated to the same iodine value, and the *mixture may be substantially* harder It is somewhat difficult, to produce a shortening with a fairly firm body at 95° to 100°F, if a straight oil is hydrogenated under *selective conditions Consequently,* if good high temperature body is desired, it may be advantageous to add sufficient vegetable stearine to the oil before hydrogenation to slightly increase its firmness at the higher temperatures Usually 2% to 5% of stearine is sufficient for this purpose

The object in the manufacture of all hydrogenated shortening is, of course, to reduce the unsaturation of the oil to the lowest possible degree which is consistent with a proper consistency in the product In order to accomplish this purpose, a great deal of care must be exercised in the *hydrogenation operation "Selectivity" is desirable in the reaction, i e,* hydrogenation should result principally in the reduction of linoleic to oleic acid, rather than of oleic to stearic acid (The stability of the product is largely dependent upon its content of linoleic acid) On the other hand, the production of iso oleic acid should be minimized, as the presence of this acid hardens the product, and limits the extent to which it can be hydro genated

The selectivity of the hydrogenation reaction and its tendency to produce iso oleic acid can both be varied considerably by varying the conditions

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have a tendency to increase the iso oleic acid In practice, conditions are chosen which will lead to moderately good selectivity combined with moderately good suppression of iso oleic acid Good products made from cottonseed oil will usually contain 8% to 14% of iso oleic acid and 3% to 8% of linoleic acid, and will have an iodine value between about 59 and 64 The most common fault in all hydrogenated shortenings is an excessive content of iso oleic acid which may in extreme cases amount to 20% or more *The iodine value of such products* may be as high as 70, or even 75

Although little or nothing is known of the factors influencing glyceride structure during hydrogenation, it is probable that the conditions favoring the production of specific fatty acids (temperature, pressure, nature of the catalyst, etc) may also favor the formation of specific configurations of the acids in the glyceride molecules This would explain the fact that different hydrogenated fats may differ *somewhat in their* physical properties even though they apparently contain identical proportions of the different *fatty* acids

In view of the probable influence of the factor of glyceride configuration, the percentage of solid (saturated and iso oleic) acids formed during hydrogenation can hardly be expected to be an absolute indication of the consistency of the hydrogenated fat Nevertheless, there is a fair correlation between the solid acids formed, and the body of the fat at 70°F The saturated acids, as would be expected, have a more pronounced hardening effect on the fat than does iso oleic acid The best correlation between consistency and solid acids formed is obtained when the effect of the saturated and iso oleic acids is weighted in favor of the former in the ratio of about 2 to 1 Such a correlation is given graphically in Figure 23 The data in this figure were obtained from batches of cottonseed oil commercially hydrogenated with different types of catalyst under a wide variety of conditions The percentage of saturated acids produced varied in

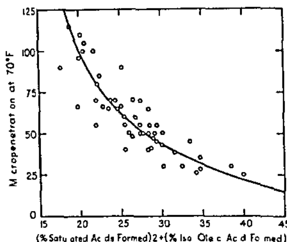


FIG 23 —Relationship between consistency at 70°F of all hydrogenated cotton seed oil shortening and solid acids formed during hydrogenation

different samples from 3 1 to 12 9, the variation in iso oleic acid formation was from 3 8% to 28 6%

Since the average micropenetration of good all hydrogenated shortenings at 70°F is about 60, it will be seen that the quantity, [(% *saturated acids produced*) 2 + % *iso oleic acids*] should not exceed about 26 in the case of shortenings made from cottonseed oil

Although the presence of iso oleic acid has a pronounced effect on the body of a hydrogenated fat at lower temperatures, it has little or no tendency to stiffen the fat at temperatures of about 90°F (32°C) and above On the other hand, saturated acids are effective in stiffening the fat over the entire range of ordinary atmospheric temperatures Consequently, the temperature at which an all hydrogenated shortening begins to soften sufficiently to lose its plastic properties is determined almost solely by the quantity of saturated acids formed during its hydrogenation The

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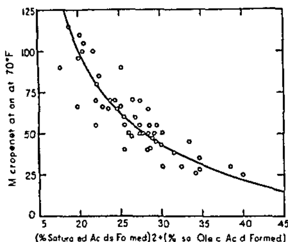


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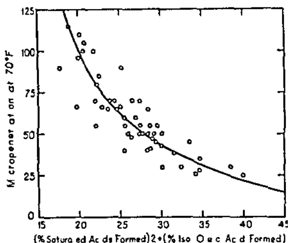


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relationship between saturated acids formed and softening point (shot melting point) in a series of hydrogenated cottonseed oil samples is shown in Figure 24 The samples of oil in this case were the same as those mentioned above, in connection with Figure 23

It will thus be seen that even if the body of an all hydrogenated shortening at about 70°F is fixed at a definite value, considerable latitude will still exist in the matter of determining its other characteristics It may be prepared with a minimum production of saturated acids and a considerable production of iso oleic acids, in this case the product will be low in linoleic acid and correspondingly stable, but its high temperature body will be poor, and it will be inclined to be brittle at low temperatures On other hand, it may be prepared in such a manner as to produce considerable amounts of saturated acids, but very little iso oleic acid The product

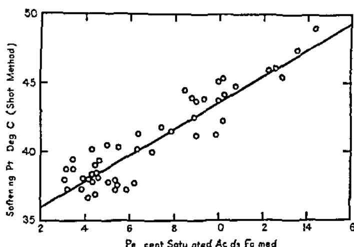


FIG 24 —Relationship between softening point of all hydrogenated cottonseed oil shortening and saturated acids formed during hydrogenation

will then have a more extensive plastic range, due to its being stiffened predominantly by saturated acids, but its stability will be decreased since saturated acids can be formed only at the expense of linoleic acid elimination

In practice, a compromise is usually effected between the mutually exclusive characteristics of high stability and long plastic range All hydrogenated shortenings which are intended for all around use are more satisfactory if neither is carried to an extreme

The stability of a hydrogenated fat depends upon the kind or kinds of oil from which it is made, the degree to which the unsaturation of the oil is reduced, and the care exercised in processing the oil

Shortenings of the general purpose type which are prepared solely from cottonseed oil usually have a keeping time by the Swift accelerated method of about 70 to 80 hours Equivalent products prepared from peanut,

soybean or sesame oil are all more stable than cottonseed oil products, and *will in general have keeping times of 100 to 200 hours* *Such stabilities* apply only to shortenings which are carefully processed Undue exposure of the shortening to oxidation at any stage in its manufacture, or contamination with soaps, oxidized oil, or other pro oxidant substances, will materially decrease its stability

The stability of a hydrogenated shortening appears to be determined *more by its content of linoleic acid than by its over all degree of unsaturation*, as measured by the iodine value The general relationship between stability and linoleic acid content is indicated in Figure 25 The data in this figure were obtained from the examination of a number of samples of hydrogenated cottonseed oil shortenings, with iodine values ranging from about 59 to 65 All were prepared in the same plant, under comparable conditions of manufacture

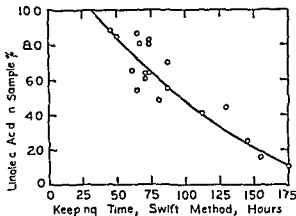


FIG 25 —Relationship between linoleic acid content of all hydrogenated cotton seed oil shortening and stability of the shortening

A large part of the all hydrogenated shortening manufactured is consumed by large commercial bakers and other users who are inclined to be highly critical of the product Obviously, for such a trade, it is necessary to produce a shortening of as even quality as is possible The manufacturers of the better brands of all hydrogenated shortenings achieve a remarkable degree of uniformity in their products, different batches of their shortenings vary but little in appearance, texture, consistency, stability, or behavior in baking operations

(g) *Biscuit and Cracker Type Shortenings*

The manufacture of crackers and sweet biscuits, to be sold in consumer s packages, presents a particular problem in stability, since long periods of shipment and storage must at times intervene between the manufacture of the article and its final consumption

Products of this type are generally baked in large establishments, which have facilities for conditioning their raw materials and conducting their dough mixing operations at any desired temperature When shortenings are handled and used under such conditions it is not necessary for them to be workable over any great range of temperature Most manufacturers of all hydrogenated shortenings accordingly make a special product for biscuits and crackers in which the plastic range of the fat is sacrificed in favor of extremely high stability

Biscuit and cracker type shortenings which are made from cottonseed oil usually have their linoleic acid content reduced to 3% or 4% or less, and have a keeping time by the Swift method of 150 to 200 hours They are relatively hard and brittle at temperatures below about 65°F, and usually either melted or nearly melted at 95° to 100°F Otherwise, they

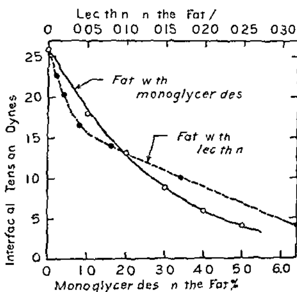


FIG 26 —Effect of mono and diglycerides (commercial) and soybean lecithin on the interfacial tension at 45°C between cottonseed oil and water

are indistinguishable from ordinary all hydrogenated shortenings Shortenings of this type are favored by some deep fat food fryers and other users in addition to biscuit and cracker makers

(h) *Superglycerinated Shortenings*

Since about 1933, a special type of all hydrogenated shortening with superior emulsifying properties has been on the market These shortenings contain a greater proportion of combined glycerol than ordinary fats, in the form of mono and diglycerides Mono and diglycerides possess ... both lipophilic (fatty acid) ... ely effective in promoting dispersion of the shortening in baker s doughs, particularly those with a high content of sugar The superior strength conferred upon the dough

by the fine dispersion of the fat enables the baker to use a higher ratio of sugar to flour and other ingredients than with ordinary shortening. This circumstance has led to the use of the term "high-ratio" as applied to these shortenings.[34] They are also described as "superglycerinated."

Superglycerinated shortenings have become extremely popular for use in cakes, sweet yeast doughs and similar products. Probably not less than 25% of the all-hydrogenated shortening normally manufactured consists of this type.

In appearance, taste, stability, etc., superglycerinated shortenings are not different from ordinary all-hydrogenated shortenings. Their content of free fatty acids is usually slightly high, amounting in various brands from 0 05% to 0 20%. The presence of free acids is claimed to be advantageous in a shortening used for cake making,[35] a slight increment of free acids naturally results from the method employed in making the mono- and diglycerides, and in some cases additional acids are apparently added.

Superglycerinated shortenings are readily recognized by their high glycerol content, and their low interfacial tension, as measured against water. They are suitable for uses other than cake making, but are not generally used for such commercially because of their high price; they usually sell for at least one cent per pound more than other shortenings. They are unsuitable for commercial deep fat frying, because of the tendency of the mono- and diglycerides to decompose at high temperatures, with the production of free glycerol, and consequent smoking.

Both the manufacture of superglycerinated shortenings and their use in cakes and similar baked goods are covered by patents Related products prepared from polyhydric alcohols other than glycerol have also been patented, as well as sulfated glycerides [36-39]

The successful use of mono- and diglycerides for the production of superior shortenings for cake making has naturally stimulated a search for other edible emulsifying agents, but so far none have been found which are particularly effective. Commercial soybean lecithin (Fig. 26) effectively lowers the interfacial tension of shortening to which it has been added, but does not confer high-ratio properties upon the shortening.

[34] The term "high-ratio" is copyrighted by the Procter and Gamble Co.

[35] V. M. Votaw and H S Coith (to Procter and Gamble Co.), U. S. Pats. 2,061,121 and 2,061,122 (1936)

[36] H. S. Coith, A S Richardson, and V M. Votaw (to Procter and Gamble Co), U S. Pats. 2,132,393-8 (1938).

[37] A. K. Epstein and B. R Harris (to Procter and Gamble Co.), U S. Pat 2,132,406 (1938).

[38] B. R. Harris, U. S Pat. 2,022,766 (1935).

[39] B R. Harris (to Procter & Gamble Co.), U. S. Pats. 2,132,416-17 and 2,132,687 (1938).

CHAPTER X

BUTTER AND MARGARINE

1. Introduction

Despite the present upward trend in the production and consumption of vegetable oils, butterfat continues to be by far the most important individual oil or fat The normal world production of butter has been reliably estimated to be as high as 4,000,000 metric tons, or 8,800,000,000 pounds annually (see pages 95-97) Thus the production of butterfat is probably twice that of any other two oils or fats combined In point of value, butterfat occupies an even more dominant position, inasmuch as it generally sells at a price much above that of ordinary edible fats

Most of the butter produced is derived from cow's milk, although there are certain sections of the world where appreciable quantities are made from the milk of other animals In India, for example, the production of buffalo butterfat or ghee is considerable The present discussion will be confined to ordinary cow's butter, particularly as it is manufactured in the United States

The manufacture of margarine or butter substitutes is a very large industry In the United States the consumption of margarine has never been high, owing to the relatively plentiful supply of butter, and the custom of consuming much fat in the form of lard or shortenings The high point of margarine consumption in this country was reached in 1919 and 1920, as a result of conditions created by preceding years of worldwide war In each of these years the per capita consumption amounted to 3 4 pounds, since then it has generally been less than 3 0 pounds In Europe the use of margarine is much more widespread, because of the relative scarcity of butter and lard, and the custom of using margarine rather than shortening for general cooking purposes In Great Britain, Germany and the Low Countries, the yearly per capita consumption varies fom 10 to 20 pounds per year In Norway it averages more than 30 pounds, and in Denmark it has been as high as 45 pounds [1]

Before proceeding to the technology of butter and margarine, an important difference may be noted between these two products Since the fat used in making margarine is a manufactured product, it is subject to

[1] K Snodgrass, *Margarine as a Butter Substitute* Food Research Institute, Stanford University, 1930

wide variations in its quality and characteristics Although the nonfatty constituents of margarine are of some concern to the margarine manufacturer, they are of minor interest in comparison with the fat On the other hand, butterfat is a natural product, and is not commonly modified by processing treatment Consequently, the technology of butter is to a large extent concerned with substances other than fat, and hence is properly the field of the bacteriologist rather than the oil and fat chemist No attempt will be made here to cover the bacteriology of butter in other than a very cursory manner

2. Butter

(a) *Production and Consumption*

Since statistics relating to the production and consumption of butter are more or less inseparable from the statistics on butterfat, the data on this product are tabulated and discussed on pages 95-98

(b) *Varieties and Grades*

The definitions which are recognized by the United States Department of Agriculture for butter and the materials from which butter are derived are as follows

Butter The food product usually known as butter and which is made exclusively from milk or cream or both, with or without common salt and with or without additional coloring matter It contains not less than 80 percent by weight of milk fat all tolerances having been allowed for

Cream That portion of milk rich in milk fat, which rises to the surface of milk on standing or is separated from it by centrifugal force

Milk The whole fresh lacteal secretion obtained by the complete milking of one or more healthy cows excluding that obtained within 15 days before and 5 days after calving or such longer period as may be necessary to render the milk practically colostrum free The name milk" unqualified means cow's milk

Butter may be produced from either sweet or ripened cream, and may be either salted or unsalted The butter produced in factories in the United States is distinguished from that produced on farms by the designation "creamery butter " The production of both sweet cream and unsalted butter in this country is limited, by far the greatest part of the creamery butter is made from ripened cream and is salted

The production of creamery butter now greatly exceeds that of farm butter in the United States, amounting in recent years to 75% to 80% of the total There are several points of difference in the manufacture of farm and creamery butter, each of which contributes to distinctive properties in the product On the farm, the cream is generally permitted to ripen spontaneously, through the action of whatever microorganisms that happen to be naturally present The common practice in creameries is to destroy

the bulk of the natural organisms in the cream through pasteurization, and conduct the ripening through the agency of special bacterial cultures, which are chosen for their ability to produce the maximum degree of aroma and flavor in the butter. Consequently, the flavor of creamery butter is more uniform and is inclined to be somewhat stronger than that of farm butter. The consistency of creamery butter is also somewhat more uniform, due to the fact that it represents the average characteristics of the fat from a larger number of different cows. Creamery butter is commonly colored artificially to a consistent yellow hue; butter made on the farm is usually not colored, and it consequently varies considerably in depth of yellow color, with the season of the year and the feed of the dairy herds.

The grade of creamery butter is assigned on the basis of a score which depends upon its flavor and aroma and its physical characteristics, as determined by inspection. The score of average good creamery butter is 92. Butter with a score of 93 or over is considered a fancy product, whereas butter scoring less than about 89 is definitely of poor quality.

A minor amount of creamery butter is produced from the butterfat remaining in the whey resulting from the manufacture of cheese. The annual production of whey butter in the United States amounts to about 25,000,000 pounds. About 2,500,000 pounds of process or renovated butter is also produced, by separating and re-emulsifying, as in margarine manufacture, the fat of butter which is off in flavor or has deteriorated badly in storage. Most of the process butter produced is either exported or utilized by commercial bakeries.

(c) *Structure and Composition*

Butter consists of a matrix of plastic fat enclosing an aqueous phase of buttermilk and water, which is dispersed in the fat in the form of very small droplets. Any salt which may have been incorporated in the butter is dissolved in the aqueous phase. The buttermilk, of course, contains a characteristic proportion of casein, minerals, and other soluble milk solids. Butter usually contains about 0.2% of phosphatides, calculated as lecithin. A small amount of air is incorporated in the fat during the operations of kneading and working. The content of air by volume usually amounts to 1% to 5%.

Butter is commonly spoken of as an emulsion. However, the fact that the fatty phase is a plastic solid rather than a liquid gives the product distinctive physical characteristics. The plasticity of butter is sufficient to prevent separation of the two phases at ordinary temperatures, even though highly effective emulsifying agents are present, in the form of proteins, phosphatides, etc. When the fat is heated, as in the frying of foods, these emulsifying agents prevent the coalescence of water droplets and

permit the water to escape quietly, with foaming of the fat, rather than spurting or spattering

The fat content of creamery butter varies according to the legal requirements in this particular in the various countries in which it is sold In the United States the fat content is usually between 80% and 81% In most of the European countries the butterfat requirements are somewhat higher, so that European butter will perhaps average 85% fat The average salt content of butter in the United States is between 2 5% and 3 0%, the butter marketed in Europe usually contains somewhat less salt *e g*, about 1% The average content of casein (curd) and other milk solids is about 1 0% The remainder of the product is, of course, water

Butter is an important source of vitamin A, and to a lesser extent of vitamin D, although the content of these two vitamins varies considerably It is considered by the Food and Drug Administration of the U S Department of Agriculture that the average vitamin A content of butter is 9000 U S P units per pound,[2] although higher values have frequently been reported (see pages 135–137) The average vitamin D content is perhaps 150 International Units per pound In uncolored butter the depth of yellow color is an indication of the vitamin A content, although this is of course not the case in butter which contains added color The vitamin A content is dependent upon the diet of the cow and is highest in the summer when the herds have access to an abundance of green fodder, which is high in carotene

(d) *Manufacture*

The manufacture of butter begins with the collection of the cream, which is for the most part separated from the milk on farms, with the aid of centrifugal separators The fat content of the cream is somewhat variable, but may be said to average about 30% to 35%

If the cream is in a sweet condition upon arrival at the creamery, it may be pasteurized and then innoculated with a suitable culture until it is fermented or "ripened" to the desired acidity For easy churning and the best flavor and keeping quality in the finished butter an acidity of about 0 25% to 0 40% calculated as lactic acid, is desired in the cream If the cream as received is higher than this in acidity, through spontaneous ripening, the excess lactic acid may be neutralized by the addition of sodium bicarbonate In the subsequent pasteurization carbon dioxide is driven off, leaving behind sodium lactate It is recommended by Golding[3] that the adjustment of acidity be done on the basis of pH rather than by titration A pH of 6 1 to 6 8 in the milk serum of butter is recommended

[2] U S National Archives *Federal Register* 6, 2761 2763 (June 7 1941)
[3] N S Golding *Proc Ann State Coll Wash Inst Dairying* 6, 37–41 (1933)

Controlled ripening at the creamery is preferable to spontaneous ripening, but is not always feasible.

The bacteria used in the controlled ripening of cream are mixed cultures of various species of *Streptococci*, especially chosen for their ability to ferment lactose and citrates, with the production of desirable flavor- and odor-giving substances. Innoculation of the cream is not carried out directly from the mother culture of bacteria, but is effected through the intermediate use of a "starter," prepared from the mother culture and relatively large batches of pasteurized milk.

For the preparation of starters either whole or skim milk may be employed. Slatter[4] recommends the use of whole milk, preferably from Jersey or Guernsey cows, because of the high content of citrates in the milk obtained from these breeds. The presence of citrates is essential because they are the precursors of the diacetyl which contributes largely to the flavor of butter. The addition of a few hundredths of a per cent of citric acid or sodium citrate is recommended by some authorities.[5,6] The fermentation of both starter and cream is carried out at relatively low temperatures (below 70°F.). The fermentation of citrates is an aerobic process; Hammer[7] suggests aeration of the milk under pressure during preparation of the starter.

The amount of starter mixed with the cream is usually about 5%, although in some cases somewhat more may be used. The production of the substances which give butter its characteristic odor and flavor occurs partly in the starter and partly after the latter is added to the cream.

After the cream is brought to the proper condition by bacterial action, it is churned in large rotary churns equipped with internal baffles, which are designed to produce splashing and concussion of the liquid, as well as simple agitation. The churning operation results in a breaking up of the fat-in-water type emulsion existing in the cream, with the resultant separation of the butterfat in the form of relatively large, coherent masses.

The physicochemical nature of the churning operation has been much debated by dairy technologists and does not yet appear to be satisfactorily explained in all particulars. The so-called foam theory of Rahn[8] has been in vogue for a considerable time. This theory accounts for the coalescence of fat globules during churning by postulating a denaturation through aeration of the surface-active materials which stabilize the globules. The more recent investigations of Palmer and Wiese[9,10] would indicate that

[4] W. L. Slatter, *Natl. Butter Cheese J.*, 28, No. 17, 38–39 (1937).

[5] M. B Michaelian, R. S. Farmer, and B. W. Hammer, *Iowa State Coll. Agr. Mech. Arts, Agr. Expt. Sta., Research Bull.*, No. 155, 325–360 (1933).

[6] H L. Templeton and H. H. Sommer, *J. Dairy Sci.*, 18, 97–104 (1935).

[7] B. W Hammer, *Dairy Bacteriology*. 2nd ed , Wiley, New York, 1938

[8] O. Rah [illegible] 1).

[9] L. S. P[illegible]

[10] H. F. [illegible]

coalescence takes place simply through a phase inversion of the emulsion, since the protein phosphatide substances which are active at the fat-water interface are largely recovered in the buttermilk

Different lots of cream vary considerably in the ease with which they may be churned The churnability of the cream depends both upon the average size of the fat globules and chemical factors which influence the surface active agents which are responsible for their stability Cream in which the globules are relatively large is correspondingly easy to churn The size of the fat globules varies with different cows and different breeds of cows Well ripened cream with considerable acidity is more easily churned than sweet cream or cream of low acidity. Palmer and Wiese,[9] who have made a study of the churnability of cream in relation to its surface active constituents, believe that the protein–phospholipide ratio may be an important factor in practical churning operations

After churning is completed, the buttermilk is drained from the butterfat and the latter is washed by a short period of agitation with cold water The washed butter is removed to working tables or machines where it is kneaded to adjust its moisture content, to incorporate salt and to improve its texture Finally, it is molded into prints and packaged

(e) *Flavor and Aroma*

The source or sources of the distinctive flavor and aroma of butter have long been a matter for discussion and conjecture Until quite recently the tendency has been to attribute butter flavor primarily to the butyric acid present in the butterfat glycerides in combination with lactic acid resulting from the fermentation of milk sugar It has also been suggested that the protein and phospholipid substances in the butter may contribute to its flavor It is now definitely established, however, that the flavor and odor is principally derived from the compound diacetyl, CH_3 CO CO CH_3, which is formed by the bacterial fermentation of citrates in the milk

The bacteriology of dairy products, in relation to the production of butter flavor and aroma, has been extensively studied by Hammer and associates,[7] who have fully elucidated the mechanism of diacetyl formation It has been demonstrated that the first product of citrate fermentation is acetylmethylcarbinol, CH_3 CO CH(OH) CH_3 This compound is relatively lacking in odor and flavor, but under the proper influences it may be oxidized to the more strongly flavored diacetyl Atmospheric oxygen is necessary for the reaction, but as pointed out by Michaelian and Hammer,[11] the latter actually is the result of bacterial action rather than chemical oxidation

Good butter cultures contain both acetylmethylcarbinol and diacetyl, they may be recognized by the creatine test[12] for the combined content of

[11] M B Michaelian and B W Hammer, *Iowa State Coll Agr Mech Arts, Agr. Expt Sta*, *Research Bull*, No 205, 203–214 (1936)

[12] B W Hammer, *J Dairy Sci*, **18**, 579–581 (1935)

these two compounds. The ratio between these two compounds in the culture itself is not a matter of particular importance, as oxidation of acetyl methylcarbinol to diacetyl will largely occur in the processes of preparing the starter and ripening the cream. The ratio of acetylmethylcarbinol to diacetyl in the finished butter is said to commonly be about 15 to 1.

The following values are given by Shrader[13] for the diacetyl content of various butters: low flavored butter, 0.1 to 0.3 p.p.m., butter of medium flavor, 0.4 to 0.8 p.p.m., full flavored butter, 0.9 to 2.0 p.p.m.

The species of *Streptococci* which are effective in the fermentation of citrates are in general distinct from those responsible for the formation of lactic acid.[5] The cultures which are used commercially are mixtures of special strains of both types which have been carefully selected for their odor- and flavor-producing characteristics.

Certain varieties of bacteria which may be present in milk and cream have the property of reducing acetylmethylcarbinol or diacetyl to 2,3-butylene glycol, $CH_3 \cdot CH(OH) \cdot CH(OH) \cdot CH_3$.[14] Such reduction is undesirable if it occurs to any considerable extent.

Other compounds known to contribute to the flavor of butter include acetic and propionic acids produced from the lactose in the milk by bacterial action.[15]

In the preparation of margarines, the same cultures are used as in the manufacture of butter and the manufacturing process involves a similar series of reactions. Yet there is a subtle difference between the flavor of margarine and butter. This would seem to indicate that the content of butyric acid peculiar to butterfat may in some way influence the development of the true butter flavor.

(f) Consistency

The iodine value and the consequent consistency of butterfat is considerably affected by the feed of the dairy herds. Since the feed necessarily varies somewhat from summer to winter, there are well defined seasonal changes in the consistency of butter. Dean and Hilditch[16] have noted the tendency of unsaturated acids in the fat to increase and saturated acids to decrease as the animals are taken off winter feeds and put on summer pasturage. These authors have also noted an increase of unsaturation in the butterfat of individual cows, as their age increases.

[13] J. H. Shrader, *Food Control*. Wiley, New York, 1939.
[14] G. L. Stahly, B. W. Hammer, M. B. Michaelian, and C. H. Werkman, *Proc. Iowa Acad. Sci.* 42, 73–76 (1935).
Agr. Expt.

The more detailed data on the effect of specific feedstuffs are from European rather than American sources, due to the greater variety of oilcakes and other concentrated feeds which are available for use in Europe The reports of Hansen and Steensberg[17] and Hansson and Oloffson[18] indicate the effect of a variety of feeds The former authors divide commercial samples of butter into three different classes, as follows (a) very soft butter, with an iodine value over 35, (b) normal butter, with an iodine value of 29 4 to 35, and (c) hard, brittle or dry butter, with an iodine value below 29 4 The feeds which tended to produce the above classes of butter were broadly as follows (a) sesame, sunflower, linseed and rapeseed cakes, soybeans, and dried corn distillery mash, (b) peanut, cottonseed and soybean cakes, potato distillery mash, barley, oats, and wheat bran, (c) coconut, palm kernel, and babassu cakes, peas and other legumes low in oil content

Of the various forms of pasturage, red clover was found to produce the softest butter,[18] with an iodine value in excess of 40 In the form of hay or ensilage, however, the softening effect of green materials was largely lost Different cows on the same rations produced butterfat varying in iodine value by as much as 6 or 7 units About 8 days of feeding on a specific ration was required to produce the characteristic effect of the feed In general the higher the iodine value of the oil in an oilcake, the softer was the butterfat However, the effect of different oils may be more closely related to their content of saturated acids than to their over all degree of unsaturation In the United States it has been generally noted that the feeding of cottonseed cake tends to produce hard butter[19, 20]

The supposedly distinctive "spreading quality" of butter has been given more attention than it deserves Actually, butter has a shorter plastic range than many other fats, and will exhibit satisfactory spreading qualities over a no more extensive range of temperatures than good vegetable margarines prepared by the hydrogenation of soft oils such as cottonseed or soybean oil The plasticity (micropenetration) curves of a sample of butter, in comparison with a typical margarine fat prepared by the hydrogenation of cottonseed oil, are reproduced in Figure 27

(g) Spoilage

Much of the spoilage occurring in butter is in a somewhat different category from that which takes place in other edible fats Whereas the deterioration of lard, shortenings and salad oils is almost wholly the result

[17] A P Hansen and V Steensberg *9th Beretning fra Statens Forsøgsmejeri*, **1931**, 95 pp [illegible]

Tierernähr , **3**, 352-391 31)

[19] E W Neasham and A J Gelpi *Natl Butter Cheese J* **25**, No 1 12-13 (1934)
[20] W D Gallup *Ind Eng Chem Anal Ed* , **8**, 123 124 (1936)

of atmospheric oxidation, bacterial and mold action may enter largely into the deterioration of butter (and margarine)

One of the reasons for incorporating salt into butter is for its preservative action. The presence of 2 5 to 3 parts of salt per 15 parts of water in the product is sufficient to inhibit the growth of microorganisms in the aqueous phase or at the water–fat interface It is probable, however, that the practice of incorporating salt in the separated butter does not result in an even distribution of salt through the product, and that some of the very small water droplets may escape contact with this preservative Bacterial action within such droplets, however, is highly localized

Deterioration of butter through oxidation is evidenced by a pronounced "tallowy" flavor This flavor appears with very slight oxidation of the fat,

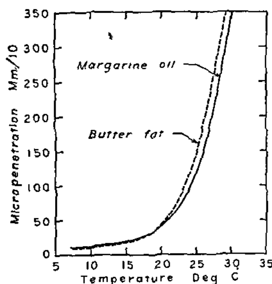


Fig 27 —Micropenetrations of the fat from typical samples of butter and all hydrogenated vegetable oil margarine

in some cases it may become evident simultaneously with the first detectable concentration of peroxides[21] Hence it must properly be regarded as an example of flavor reversion rather than oxidative rancidity The flavor reversion of butterfat, like that of other fats and oils, appears to be associated with the presence of highly unsaturated fatty acids There do not appear to be more than traces of linolenic acid in butterfat,[22, 23] but the presence of highly unsaturated C_{20} and C_{22} acids has been reported[2?]

At times, the reverted flavor of butter is of a decidedly fishy character

[illegible] (1937)

15–134 (1933) T P

The subject of fishy flavor has been investigated by Davies and Gill,[24] who ascribe fishiness to trimethylamine derived from phosphatides in the fat For some reason as yet unknown, highly unsaturated fatty acids in the fat are necessary for the development of fishy flavor

True oxidative rancidity in butter is rarely encountered partly because of the fact that the over all degree of unsaturation in the fat is low, and partly because oxidation is very slow at the low temperatures at which butter is stored At true cold storage temperatures, butter deteriorates very little and may be satisfactorily stored for months

3 Margarine

(a) *History*

Margarine was invented during the Franco Prussian War by the French chemist, Mége Mouriés It won for the inventor a prize offered by Napo leon III for a satisfactory butter substitute The award of the prize was made in 1870 By 1872 the product appears to have attained commercial importance in France and shortly thereafter it was being produced in a number of other countries including the United States

The original process for making margarine involved the following suc cessive steps (*a*) the low temperature rendering of beef fat, (*b*) fractional crystallization of the rendered fat to yield a fraction of lower melting point than the original fat and (*c*) the production of a butterlike flavor by mixing this fraction with milk and digesting the mixture with tissues from cows' udders

The final step was apparently intended to imitate the natural body pro cesses of the cow in the belief that butterfat was formed from the body fat of the animal by the action of substances present in the udder This belief was of course in error No such transformation of fat is possible and such butterlike flavor as the product possessed could only have been derived from the action of bacteria in the milk However, the principle of *treating* fats other than butterfat with milk to produce the flavor of butter was established even though by accident

The improvements which were subsequently introduced in the original Mége Mouriés process have been traced in some detail by Snodgrass [1] The use of mammary tissues in the preparation of margarine was probably abandoned at a relatively early date Shortly thereafter it was discovered that a more pronounced flavor of butter could be imparted to the product by souring or ripening the milk before incorporating it with the fat, and the use of previously soured milk became the accepted practice Eventually it was found that certain strains of milk souring bacteria produced a more

[24] W L Davies and E Gill *J Soc Chem Ind* 55 141–146T (1936)

pleasing aroma in butterfat than did others, and the use of pure cultures for ripening cream for butter manufacture became general When the same cultures were employed for fermenting the milk to be incorporated into margarine, an improvement in the flavor of this product was also obtained Consequently, the spontaneous souring of the milk was abandoned in favor of controlled fermentation by butter cultures

The first important improvement in the process, from the standpoint of the physical properties of the product, was the introduction of a method of quickly solidifying the fat, in order to avoid the formation of large crystals, with consequent graininess and poor consistency in the fat The first method of margarine solidification involved simply running the emulsion of milk and liquid fat in a slow stream into a vat of chilled water This method was in vogue for many years and it is only quite recently that it has been largely replaced by the chill roll and Votator methods of solidification, in which the fat is crystallized by contact with a refrigerated metal surface

According to Snodgrass,[1] the techniques of employing both rapid crystallization and previously soured milk were first described by Mott, in the United States, and were in commercial use in this country as early as 1877

Milk in combination with fat alone does not have a sufficient content of surface active materials to produce an emulsion of the same stability as that existing in butter Much of the literature of margarine manufacture pertains to the use of various added substances to promote emulsification Margarine which contains insufficient emulsifying agents not only is inclined to be "leaky" in storage, but also does not behave properly in cooking Its deficiencies in comparison with butter are particularly noticeable in frying where the ready separation of its water and fat phases causes the margarine to spatter, and also causes the curd or milk solids to adhere to the frying pan

Probably the first added emulsifying agent to be used in margarine in any quantity was egg yolk A German patent covering the use of this material was granted in 1884[1] Since the introduction of the Bollman process[25] for the production of relatively cheap vegetable phosphatides from soybeans, vegetable lecithin has largely replaced egg yolk, however The addition of glucose to margarine to produce foaming and browning is said to be common in Europe In the United States, large quantities of synthetic emulsifying agents, such as mono and diglycerides, and sodium monostearin sulfoacetate, are used

In margarine solidified by the modern Votator process a very fine dispersion of the aqueous phase may be obtained, which practically eliminates "leaking" or "weeping" of the product even in the entire absence of an

[25] H Bollmann Brit Pat 2ٍ9 16C (1925)

emulsifying agent An antispattering agent is desirable in such margarine, however

Inasmuch as the chief nutritional deficiency of margarine, as compared with butter, resides in its negligible content of vitamin A, it is natural that margarine manufacturers should have given consideration to the addition of concentrates of this vitamin to their products The addition of both vitamins A and D to margarine has been practiced in Europe for some years, but until very recently such addition was illegal in the United States In 1941 a ruling of the Federal Security Administration permitted the addition of vitamin A equivalent to its normal content in butter, and since that time most of the margarine marketed in the United States has contained 9000 or more U S P units of this vitamin per pound

(b) *Margarine Legislation*

The invention of margarine has made it possible to prepare a product very similar to butter from oils and fats which are much less expensive than butterfat Hence the trade in margarine offers peculiar opportunity for the practice of fraud upon the consumer, who may be sold margarine under the impression that he is being supplied with butter At the same time, the sale of margarine under any circumstances may be considered inimical to the interests of the dairy industry because of the relative cheapness with which this product may be manufactured These two considerations have given rise to much legislation governing the production and distribution of margarine No attempt will be made here to review the involved and controversial subject of margarine legislation in any detail, but a few salient points may be briefly mentioned

In Europe there has in general, been little tendency to apply legal restrictions to the production of margarine Legislation has been chiefly aimed at providing the consumer the protection which might reasonably be expected in any similar foodstuff The product is generally required to be adequately labeled as to quality and identity, a minimum fat content is specified sanitary standards are enforced, and in some cases a small amount of starch or sesame oil must be added to provide a ready means of detecting the adulteration of butter with margarine In the United States on the other hand the consumption of margarine is severely limited by the imposition of excise taxes which are frankly designed to minimize the competition offered by this product to the dairy industry

The present federal excise tax on margarine amounts to 0 25 cent per pound on uncolored margarine and 10 cents per pound on yellow colored margarine Through a number of administrative rulings and court decisions it has been established in principle that margarine must be considered colored if it is noticeably yellow in hue, irregardless of whether the color is

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[25] H Bollmann Brit Pat 259 166 (1925)

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derived from artificial dyes or from the natural color of the constituent oils The result of these taxes has been to virtually eliminate from the market margarine which has been colored by the manufacturer A small portion of yellow coloring material is customarily included with each print of margarine sold, but it may legally be incorporated with the fat only by private individuals, for the personal use of their own families

The federal oleomargarine act under which the product is taxed is under the administration of the Bureau of Internal Revenue of the U S Treasury Department Retail dealers are not permitted to repack margarine or to disperse it from large containers, but must sell it from the manufacturers' original packages, which cannot contain more than 10 pounds each Actually, practically all margarine is sold at retail in the form of one pound prints The internal revenue stamps, however, are not affixed to the original prints, but to the cartons in which they are packed by the manufacturer The yearly license fees which are imposed by the Federal Government are as follows manufacturers, \$600, wholesalers, \$480 for the sale of colored and \$200 for the sale of uncolored margarine, retailers, \$48 for the sale of colored and \$6 for the sale of uncolored margarine

In addition to the federal taxes many of the individual states have laws imposing penalties upon the sale of margarine, either in the form of outright taxation or heavy license fees The taxes is some states are so high (5 to 15 cents per pound) as to virtually prohibit trade in the commodity

The legal definition of margarine, as established by Act of Congress, is very broad, and embraces any plastic fat composition emulsified with moisture in excess of 1%, with the exception of water churned puff paste shortening, which is specifically exempted from the provisions of the act, provided that its melting point is in excess of 118°F

Other federal legislation which affects the manufacture of margarine includes the Federal Food, Drug, and Cosmetic Act This act provides for the establishment of a definition of margarine, *in terms of its* various ingredients, and forbids the use of ingredients not specifically included in the definition The definition and standard of identity for margarine, as promulgated by the Federal Security Administration, June 15, 1941, under the provisions of the Federal Food, Drug, and Cosmetic Act, is as follows

(*a*) Oleomargarine is the plastic food prepared with one or more of the optional fat ingredients named under one of the following subparagraphs (*1*) (*2*) (*3*) or (*4*)

(*1*) The rendered fat, or oil, or stearin derived therefrom (any or all of which may be hydrogenated), of cattle sheep, swine, or goats, or any combination of two or more of such articles

(*2*) Any vegetable food fat or oil, or oil or stearin derived therefrom (any or all of which may be hydrogenated) or any combination of two or more of such articles

(*3*) Any combination of ingredients named under subparagraphs (*1*) and (*2*) in such proportion that the weight of the ingredients named under (*1*) either equals the weight of the ingredients named under (*2*), or exceeds such weight by a ratio not greater than 9 to 1

(4) Any combination of ingredients named under subparagraphs (1) and (2) in such proportion that the weight of the ingredients named under (2) exceeds the weight of the ingredients named under (1) by a ratio not greater than 9 to 1.

One of the five following articles is intimately mixed with the fat ingredient or ingredients, after such article has been pasteurized and subjected to the action of harmless bacterial starters (i) cream, (ii) milk, (iii) skim milk, (iv) any combination of dried skim milk and water in which the weight of the dried skim milk is not less than 10 percent of the weight of the water or (v) any mixture of two or more of these (The term "milk" as used herein means cow's milk) Congealing is effected, either with or without contact with water, and the congealed mixture may be worked In the preparation of oleomargarine one or more of the following optional ingredients may also be used

(5) Artificial coloring

(6) Sodium benzoate, or benzoic acid or a combination of these, in a quantity not to exceed 0 1 percent of the weight of the finished product

(7) Vitamin A added as fish liver oil or as a concentrate of Vitamin A from *fish liver oil (with any accompanying Vitamin D and with or without added Vitamin* D concentrate) in such quantity that the finished oleomargarine contains not less than 9 000 United States Pharmacopoeia Units of Vitamin A per pound

(8) The artificial flavoring diacetyl added as such, or as starter distillate, or produced during the preparation of the product as a result of the addition of citric acid or harmless citrates

(9) (i) Lecithin in an amount not exceeding 0 5 percent of the weight of the finished oleomargarine or (ii) monoglycerides or diglycerides of fat-forming fatty acids or a combination of these, in an amount not exceeding 0 5 percent of the weight of the finished oleomargarine or (iii) such monoglycerides and diglycerides in combination with the sodium sulfo-acetate derivatives thereof in a total amount not exceeding 0 5 percent of the weight of the finished oleomargarine, or (iv) a combination of (i) and (ii) in which the amount of neither exceeds that above stated, or (v) a combination of (i) and (iii) in a total amount not exceeding 0 5 percent of the weight of the finished oleomargarine (The weight of diglycerides in each of ingredients (ii), (iii) (iv) and (v) is calculated at one-half actual weight)

(10) Butter

(11) Salt

The finished oleomargarine contains not less than 80 percent fat, as determined by the method prescribed in "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," 4th Edition, 1935, page 289, or 5th Edition 1940 page 298 under Indirect Method—Official "

(b) When any ingredient named under one of the following specified subparagraphs of paragraph (a) is used, the label shall, except as hereinafter provided, bear the statement set forth below after the number of such subparagraph

Subparagraph (1) Prepared from Animal Fat," or "Made from Animal Fat "

Subparagraph (2) "Vegetable," or "Prepared from Vegetable Fat," or "Made from Vegetable Fat "

Subparagraph (3) "Prepared from Animal and Vegetable Fats," or "Made from Animal and Vegetable Fats "

Subparagraph (4) "Prepared from Vegetable and Animal Fats," or "Made from Vegetable and Animal Fats "

Subparagraph (5) "Artificially Colored," or "Artificial Coloring Added," or "With Added Artificial Coloring "

Subparagraph (6) "Sodium Benzoate (or, as the case may be, 'Benzoic Acid' or 'Sodium Benzoate and Benzoic Acid') Added as a Preservative," or "With Added

Sodium Benzoate (or, as the case may be, 'Benzoic Acid' or Sodium Benzoate and Benzoic Acid') as a Preservative "

Subparagraph (7) "Vitamin A Added," or "With Added Vitamin A "

Subparagraph (8) "Artificially Flavored," or "Artificial Flavoring Added," or "With Added Artificial Flavoring "

Where oil is used, the word "oil" may be substituted for "fat" in the label statement In lieu of the word "animal" or "vegetable" in any such statement, the common or usual name of the fat ingredient subparagraphs (5), (6), (7), and (8) are used, the words "added" or "with added" need appear only once, either at the beginning or end of the list of such ingredients declared The declaration of Vitamin A may include the number of United States Pharmacopoeia Units which have been added

Whenever the name oleomargarine" appears on the label so conspicuously as to be easily seen under customary conditions of purchase, the words and statements here prescribed showing ingredients used shall immediately and conspicuously precede or follow, or in part precede and part follow, such name, without intervening written, printed, or other graphic matter

(c) Production and Consumption

The production and consumption of margarine in the United States during recent years is indicated in Table 101

During the year beginning in July, 1941, the United States margarine production was distributed among the various states as follows Illinois, 29%, California, 14%, Ohio, 14%, New Jersey, 8%, Indiana, 7%, Texas, 7%, Kansas, 6%, Michigan, 5%, and other states, 10%

The average wholesale price of domestic vegetable margarine at Chicago, during the month of January of recent years, has been as follows (in cents per pound) 1937, 16 5, 1938, 15 5, 1939, 14 5, 1940 15 0, 1941, 14 5, 1942, 18 5, and 1943, 19 0

Recent data on the consumption of margarine in the European countries are not available However, in past years the per capita figures for Great Britain, Germany, the Netherlands, Belgium, and Sweden have been between 12 and 20 pounds annually Consumption is extremely high in both Denmark and Norway Both Italy and France have a per capita consumption smaller than that of the United States, as probably also have Russia and most of the central European countries The margarine industry is also relatively undeveloped in Canada and Central and South America, and is virtually nonexistent in any part of Asia or Africa

It is a somewhat curious fact that the consumption of margarine is highest in the sections of Europe which produce butter in the greatest quantity The dairy farmers in these sections are inclined to sell their butter, and eat instead the cheaper oleomargarine A similar tendency has been noted in the United States [1] The consumption of margarine is apparently highest in the Middle Western States and on the Pacific Coast, where the dairy industry is highly developed

(d) Fats for Margarine Manufacture

Preference for margarine fats in the United States has passed through three well-defined stages

As noted previously, the first margarine was made from oleo oil, prepared by the fractional crystallization of beef fat Oleo oil is by itself quite similar in physical properties to butter It is firm at low temperatures,

TABLE 101
PRODUCTION AND CONSUMPTION OF MARGARINE IN THE U S (1912-1942)*

Year	Production million pounds	Exports million pounds	Consumption	
			Total million pounds	Per capita pounds
1912	142.2	2.8	138.8	1.5
1913	152.0	2.4	149.9	1.6
1914	141.2	1.8	138.9	1.4
1915	142.0	3.5	138.8	1.4
1916	187.6	2.7	183.4	1.8
1917	287.2	2.7	283.7	2.8
1918	350.6	3.0	346.9	3.3
1919	368.8	15.4	353.9	3.4
1920	369.5	6.1	363.7	3.4
1921	215.1	1.5	214.6	2.0
1922	181.8	1.1	183.5	1.7
1923	227.6	1.5	226.3	2.0
1924	231.8	1.2	230.5	2.0
1925	231.0	1.3	232.1	2.0
1926	212.6	1.9	210.5	2.1
1927	277.5	1.0	275.7	2.3
1928	316.7	2.0	314.0	2.6
1929	356.2	2.2	352.9	2.9
1930	325.7	1.9	323.3	2.6
1931	229.9	1.8	230.0	1.9
1932	203.2	1.6	201.7	1.6
1933	215.5	1.5	212.9	1.9
1934	264.4	1.6	263.2	2.1
1935	381.6	1.4	379.9	3.0
1936	393.3	1.2	391.0	3.0
1937	397.4	0.3	397.3	3.1
1938	385.2	0.2	385.2	3.0
1939	300.9	0.3	301.2	2.3
1940	320.4	—	318.6	2.4
1941	367.6	—	364.2	2.7
1942	425.7	—	365.0	2.7

* From reports of the U S Bur Agr Economics

and yet, like butter, melts readily in the mouth Later, oleo oil was supplemented by neutral lard, which in reasonable proportions occasioned no harm to the body of the product, or even improved it, by slightly extending its plastic range For many years these two animals fats continued to be the principal raw materials used in margarine manufacture Vegetable oils were little used, partly because most of them were too soft to be included in margarine in any quantity, and partly because refining and

deodorizing processes were not sufficiently developed to permit the production of a fat with a neutral flavor from vegetable materials

During the years 1914 to 1919, deodorized coconut oil began to be much used in margarine Coconut oil, palm kernel oil, babassu oil, etc, are somewhat more brittle than oleo oil or mixtures of oleo oil and neutral lard at the lower temperatures, and also have a somewhat lower melting point However, if their plastic range is extended somewhat, by the inclusion of minor proportions of a liquid oil, and oleo stock, oleostearine, or hydrogenated oil, they have a suitable consistency for margarine manufacture The use of coconut oil increased rapidly, and by 1929 this oil constituted over 60% of the total fats and oils used in the industry

Since about 1934, the relative volume of coconut oil consumed by the margarine industry has declined, and there has been a corresponding increase in the use of hydrogenated cottonseed and soybean oils This latter shift in raw materials may be attributed in part to the imposition of new federal processing taxes on coconut and other foreign oils in 1934, and in part to a general advance in oil and fat technology Previously, cottonseed soybean and similar oils had been used to some extent in margarine but seldom as the sole or principal fatty ingredients of the product Although fats suitable for the manufacture of shortenings had been prepared from such oils for many years by hydrogenation many margarine manufacturers, who were relatively unfamiliar with this process, were inclined to believe that fat of the proper consistency for margarine could not be prepared by hydrogenation of a liquid oil Subsequent experience demonstrated that the body of properly prepared hydrogenated products was even superior to that of margarine made from oleo oil, coconut oil, or other natural fats In addition, the hydrogenation technique permitted the manufacture of fats which were very stable, absolutely neutral in flavor, and highly uniform in consistency At the present time, most of the margarine of the highest grade made in the United States is a hydrogenated vegetable oil product

The trends in margarine fat consumption in the United States during the past twenty five years are indicated in Table 102

In many respects, the trend of consumption of the various margarine fats has run a course in Europe parallel to its course in the United States There, too, the use of animal fats has declined greatly from its previous high point Prior to 1914, oleo oil exported from the United States was one of the major ingredients of European margarine In 1908, exports of oleo oil for this purpose reached a record volume of 212,000 000 pounds After 1924, however, exports declined to less than 100,000,000 pounds yearly, and since 1934 they have not exceeded 10,000,000 pounds in any one year

Coconut, palm kernel, and babassu oils were used in large quantities in

Europe before they became very popular in the United States. The large scale use of hydrogenated cottonseed, soybean and peanut oils in Europe also antedated the use of these oils in the United States. Manchurian soybean oil, in particular, was imported into Germany in large quantities prior to 1914, and was principally consumed by the margarine industry.

TABLE 102

FATS AND OILS IN MILLION POUNDS USED IN THE MANUFACTURE OF MARGARINE IN THE U. S. (1917–1942)

Oil or fat	1917*	1922*	1927	1932	1937	1942
Oleo oil	96.7	11.0	49.5	12.5	12.3	22.5
Neutral lard	42.4	27.1	25.0	9.4	1.8	8.1
Oleostearine	2.5	4.6	5.4	3.7	3.1	2.0
Other animal fats	3.5	3.1	4.6	0.5	1.3	4.1
Coconut oil	19.8	57.4	122.6	123.2	73.8	3.5
Palm kernel oil	—	—	—	—	7.9	—
Babassu oil	—	—	—	—	14.6	0.3
Cottonseed oil	63.7	15.4	21.6	15.1	173.6	166.4
Soybean oil	—	—	—	—	31.8	133.3
Peanut oil	10.5	11.6	4.7	2.5	2.0	0.9
Other vegetable oils	0.8	0.0	0.8	0.3	2.8	5.0

* Fiscal years beginning July 1, data for other years are for the calendar year.

TABLE 103

OILS AND FATS IN MILLION POUNDS USED IN THE PRODUCTION OF MARGARINE IN THE UNITED KINGDOM AND GERMANY

Oil or fat	United Kingdom (1937)	Germany* (1935)
Whale oil	148	470
Beef fat	18	11
Hog fat	2	4
Cottonseed oil	31	—
Peanut oil	69	29
Soybean oil	0	60
Coconut oil	60	99
Palm kernel oil	22	126
Other oils	11	69

* Includes about 10% of edible fats not used in margarine.

In later years hydrogenated whale oil came to be the most important single ingredient of European margarine. Probably much more than half of the annual whale oil production of about 1,250,000,000 pounds was regularly used for this purpose. Among the other fats and oils, palm kernel oil has been particularly favored in Germany, whereas British margarine manufacturers have been more inclined to the use of cottonseed and peanut oils. The oils and fats used in the United Kingdom and Germany in typical years prior to 1939 are listed in Table 103.

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Since about 1934, the relative volume of coconut oil consumed by the margarine industry has declined, and there has been a corresponding increase in the use of hydrogenated cottonseed and soybean oils This latter shift in raw materials may be attributed in part to the imposition of new federal processing taxes on coconut and other foreign oils in 1934 and in part to a general advance in oil and fat technology Previously, cottonseed, soybean and similar oils had been used to some extent in margarine, but seldom as the sole or principal fatty ingredients of the product Although fats suitable for the manufacture of shortenings had been prepared from such oils for many years by hydrogenation, many margarine manufacturers, who were relatively unfamiliar with this process, were inclined to believe that fat of the proper consistency for margarine could not be prepared by hydrogenation of a liquid oil Subsequent experience demonstrated that the body of properly prepared hydrogenated products was even superior to that of margarine made from oleo oil, coconut oil, or other natural fats In addition, the hydrogenation technique permitted the manufacture of fats which were very stable, absolutely neutral in flavor and highly uniform in consistency At the present time, most of the margarine of the highest grade made in the United States is a hydrogenated vegetable oil product

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TABLE 102

FATS AND OILS IN MILLION POUNDS USED IN THE MANUFACTURE OF MARGARINE IN THE U S (1917–1942)

Oil or fat	1917[a]	1922[a]	1927	1932	1937	1942
Oleo oil	96 7	41 0	49 5	12 5	12 3	22 5
Neutral lard	42 4	27 1	25 0	9 4	1 8	8 1
Oleostearine	2 5	4 6	5 4	3 7	3 4	2 9
Other animal fats	3 5	3 1	4 6	0 5	1 3	4 1
Coconut oil	19 8	57 4	122 6	123 2	73 8	3 5
Palm kernel oil	—	—	—	—	7 9	—
Babassu oil	—	—	—	—	14 6	0 3
Cottonseed oil	63 7	15 4	24 6	15 1	173 6	166 4
Soybean oil	—	—	—	—	31 8	133 3
Peanut oil	10 5	11 0	4 7	2 5	2 9	0 9
Other vegetable oils	0 8	0 0	0 8	0 3	2 8	5 0

[a] Fiscal years beginning July 1, data for other years are for the calendar year

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Oil or fat	United Kingdom (1937)	Germany[a] (1935)
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Peanut oil	69	29
Soybean oil	0	60
Coconut oil	60	99
Palm kernel oil	22	126
Other oils	11	69

[a] Includes about 10% of edible fats not used in margarine

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(e) Flavor

The flavor of good margarine is very similar to, but not altogether identical with that of butter Properly speaking, none of natural flavors of fats and oils have any place in margarine It is desirable for magarine fat to be completely neutral Carefully rendered oleo oil or neutral lard is sufficiently free from flavor to be reasonably suitable for margarine, although now it is not uncommon for even these fats to be deodorized, in some cases after slight hydrogenation, before they are used for this purpose It is necessary for vegetable oils to be very completely deodorized for margarine manufacture, as their natural flavor is more foreign to this product than is that of the animal fats mentioned above

Coconut oil and the other oils of the lauric acid type are flavorless when properly deodorized and are stable toward oxidation, hence are entirely suitable margarine fats Otherwise, the oils which may be hydrogenated for the production of good margarine fats are the ones which are likewise suitable for the manufacture of high grade all hydrogenated shortenings Cottonseed, peanut, sesame, sunflower, palm oil, and other oleic linoleic acids oils may be used in margarine in practically any combination or in any proportions Hydrogenated soybean oil contributes a slight foreign flavor to the product if it is present to the extent of more than 25% to 30% Other oils of the linolenic acid group are relatively poor margarine oils as is rapeseed oil Fish oils are not suitable materials for the preparation of hydrogenated margarine fats, as they invariably revert in flavor except when hydrogenated virtually to the form of stearine Hydrogenated whale oil is greatly superior to fish oil, and is much used in margarine manufacture in Europe Data relative to the actual procedure followed in hydrogenating whale oil for this purpose are unavailable, but it may be assumed that much care must be exercised to avoid excessive flavor reversion in this oil also

Much of what has been said previously regarding the flavor of butter is applicable to margarine also The same bacterial cultures are used for preparing milk for margarine manufacture as are employed in the ripening of cream for buttermaking, and it is probable that the reactions which take place are quite similar It is noteworthy that the best flavor in margarine is produced by allowing bacterial action to take place after the ripened milk is emulsified with the fat Thus the presence of a fatty phase appears to in some way promote the development of a butterlike flavor The incorporation of salt in the emulsion inhibits bacterial action, consequently it is preferable to allow some time between the solidification of the emulsion and the addition of salt In the older processes in which the emulsion was solidified in cold water or on a chill roll this was easily accomplished by merely storing the product for 24 to 48 hours before it was salted and printed Special arrangements must be made, however, in using the

modern Votator process, in which the emulsion is solidified and formed into prints in one continuous operation Lately the addition of diacetyl to margarine as a flavoring material has become quite common

There is a wide variation in the flavor and general quality of margarines made in the United States Some inferior products have a pronounced fat flavor and little flavor due to the milk used in their manufacture In the better margarines, however, fat flavor is entirely absent, the butterlike flavor is strong and by the layman the product can be distinguished from good butter only with difficulty

(f) Consistency

There is perhaps no plastic fat product in which the matter of consistency is of such importance as in margarine One essential qualification of table margarine is that it shall melt readily and with practical completeness in the mouth In this respect there is an essential difference between margarine and shortenings Whereas shortenings are invariably consumed in the molten form, in various hot dishes, or else finely dispersed in pastries, etc , margarine, like butter, is for the most part spread on bread and taken into the mouth in more or less gross portions A residue which fails to melt at body temperature may not be noticeable in a shortening—in fact, such a residue is necessary if the product is to have high temperature body—but in margarine it imparts an undesirable "pasty" sensation in the mouth

At ordinary temperatures, margarine should be plastic and should spread freely At refrigerator temperatures, however, it is desirable for margarine to be quite hard and firm This is partly because butter is firm under the same circumstances, and partly because a rather firm body is required in order for the product to be easily formed into the blocks or "prints" in which it is customarily marketed

On the whole, the manufacturer of margarine is inclined to pattern the consistency of his product after that of butter, although it may be conceded that at temperatures of about 45° to 60°F butter is rather harder and more brittle than is strictly desirable

The consistency of margarine is principally dependent upon the fats used in its manufacture and is influenced but little by ordinary variations in methods of solidifying and emulsifying the product, or by variations in the relative proportions of milk and fat

Where such ingredients as oleo oil, oleo stock, neutral lard, coconut oil palm kernel oil babassu oil, etc , are used in preparing the margarine fat, the proper consistency is obtained by blending the various fats in the proper proportions If the fat is to be prepared by the hydrogenation of a normally liquid oil, however, the more usual practice is to attain the proper consistency by a single, carefully controlled hydrogenation The practice of blending fats of different degrees of hardness is not advantageous in the

manufacture of all hydrogenated margarines In such margarine it is a matter of some difficulty to hydrogenate the oil to a sufficient degree of firmness at low temperatures without exceeding the desired melting point, and mixtures or blends of hydrogenated oils are invariably less satisfactory in this particular than a single hydrogenated oil

The foregoing considerations apply, of course, only to table margarine Pastry margarines, which are used for cooking, are not required to melt at body temperature Margarines of the puff pastry type are, in fact, the highest melting of all edible fat products The puff pastry fat most commonly sold in the United States is made from 35% of oleostearine blended with 65% of cottonseed oil, and has a melting point in excess of 118°F A tough, waxy body is essential in this product, in order to make it extensible in the "rolling in" process used in making puff pastry

(g) *Surface Active Agents*

As mentioned previously, it is necessary to add special emulsifying agents to margarine in order to confer upon it the physical properties of the butter emulsion Margarine prepared without the use of added agents is inclined to "leak" or exude the aqueous phase while in storage, unless manufacturing methods have been employed which yield a very tight emulsion Also, when used in cooking, and particularly in frying, the behavior of untreated margarine is quite different from that of butter

The emulsifying agents naturally present in butter effectively prevent the coalescence of water droplets even after the emulsion is heated Under these circumstances, the volatilization of water in the frying process occurs from a multitude of very small droplets, with the appearance of quiet foaming, and without the milk solids settling to the bottom of the frying pan In margarine, however, unless added emulsifying agents are present, there will be a marked tendency for the small water droplets to unite to form large drops upon the application of heat The generation of steam from such large drops is sufficiently violent to eject particles of oil from the cooking vessel, or in other words, to cause spattering Also, the milk solids or curd tend to settle out of the aqueous phase and become adherent to the bottom of the vessel

A wide variety of substances has been suggested for addition to margarine to improve its emulsifying properties The use of egg yolk for this purpose was probably quite common in Europe at one time Lately, however, it has been more or less completely supplanted by soybean lecithin [26-27] Lecithin has never been used in margarine in the United States to the extent to which it has been employed in Germany and other European countries, although 278,000 pounds were reported used for this purpose in

[26] Hanseatische Muhlenwerke A G , German Pat 576 102 (1933)
[27] B Rewald, U S Pat 1,895 424 (1933)

1942 Lecithin is usually used in an amount not exceeding 0 5% of the weight of the fat

Another emulsifying agent which has been considerably used, especially in Europe, is the so called "Paalsgaard emulsion oil" of Schou,[28] which consists of soybean oil which has been oxidized and polymerized for the production of hydrophilic groups

The present tendency in the United States is toward the use of synthetic surface active agents prepared from a glyceride or fatty acid base Ordinary mono- and diglycerides, as prepared for incorporation into superglycerinerated shortenings are quite effective "antileaking" agents in a concentration of a few tenths of one percent, but have little, if any effectiveness as "antispattering" agents The sodium sulfoacetate derivatives of the mono and diglycerides, however, are very effective antispattering agents, and are widely used as such

The effectiveness of the latter class of substances in preventing spattering is explained by Harris[29] on the basis of a proper balance between hydrophilic and lipophilic groups in the molecule

The various synthetic substances (with the exception of monostearine) are classified together by the Bureau of Internal Revenue as "glycerine derivatives," of which 823,000 pounds were consumed in 1942, in the manufacture of 425,700,000 pounds of margarine During the same year there was a consumption of 187,000 pounds of monostearine

(h) Manufacture

The manufacture of margarine begins with preparation of the margarine fat The only fats which are used in margarine without processing treatment are neutral lard, and oleo stock and its derivatives, oleo oil and oleo stearine In order to be suitable for margarine, these fats must be rendered and subsequently handled with extreme care Only very fresh fatty tissues can be rendered, and the rendering operation must be carried out at a low temperature in order to avoid the production of oxidized or cooked flavors in the expressed fat After the fat is prepared, it should preferably be made up into margarine with reasonable promptness The flavor of neutral pork and beef fats is very easily damaged by slight oxidation, and prolonged storage or repeated melting or heating of the fats during storage or processing is extremely detrimental to their quality These fats are most successfully handled by meat packing plants which are engaged in both rendering and margarine manufacturing operations, so that the fats can be promptly transferred from one department to the other

Recently, since processing facilities for hydrogenation and deodorization have become more generally available, it has become quite common practice

[28] E V Schou, Brit Pats 187 298–99 (1921) U S Pat 1,570 529 (1926)

[29] B R Harris, U S Pats 1,917,249–60 (1933)

to subject animal fats to alkali refining and slight hydrogenation, followed by deodorization, before they are incorporated into margarine This practice enables the manufacturer to utilize fats which have been stored or have otherwise slightly deteriorated in flavor, and results in a product which is markedly superior in stability to margarine made from even the highest grade unhydrogenated fats Deodorization of either hog or beef fat is much more successful if it is preceded by hydrogenation, the flavor of these fats is unstable if they are deodorized without previous treatment

In the case of oleo oil, slight hydrogenation under selective conditions does not harm the consistency of the fat, in fact, such alteration in consistency as does occur may be considered desirable, inasmuch as margarine made from ordinary oleo oil is inclined to be somewhat too soft at the higher temperatures In the case of lard, however, even careful hydrogenation is likely to result in the production of a small proportion of fully saturated glycerides These glycerides leave a residue which does not melt in the mouth, hence if the hydrogenated lard is used in large amount in margarine, the latter will be inclined to be "pasty " The hydrogenated lard can, however, be converted to an entirely suitable margarine fat by removing its high melting glycerides by fractional crystallization This latter process is rather simply carried out, inasmuch as the high melting portions separate in the form of rigid easily filterable crystals, and do not constitute more than a few per cent of the original fat The entire process may be carried out by hydrogenating alkali refined lard, with an iodine value of about 68 to an iodine value of 60, graining out about 10% of the fat by holding it for 24 hours at 94°F and separating the liquid portion by filtration in an ordinary filter press

In preparing margarine oil from cottonseed soybean, and other liquid oils by hydrogenation, the latter process should be carried out under highly *selective conditions, in order* to harden the oil properly without producing in it an excessive amount of fully saturated, high melting glycerides If the hydrogenation is not carried out properly, an oil with the proper melting point and high temperature consistency will be too soft to print properly, and conversely, an oil which is sufficiently firm at 40° to 60°F will be pasty in the mouth

Efficient, high temperature deodorization is necessary for oils or hydrogenated oils of the oleic linoleic acid type which are to be used in margarine

Coconut oil or other oils of the lauric acid type are, like the oleic linoleic acid oils, refined and deodorized for margarine manufacture, but are not usually hydrogenated These oils are best blended with a certain proportion of both soft oils and hard fats to improve their plastic range, as alone they soften and melt too abruptly

Pastry or cooking margarines may be prepared from a somewhat greater variety of materials than ordinary table margarines, as in these products

it is not necessary for the fat to melt cleanly in the mouth The consistency of these margarines covers a considerable range according to the preferences of the particular trade for which they are designed and is controlled by suitably varying the proportions of the various fatty ingredients or the conditions of the hydrogenation process Puff paste fat which in the United States is not officially designated as a margarine because of its high melting point (over 118°F) is usually made by compounding 35% of oleo stearine with 65% of deodorized cottonseed oil and emulsifying this fat with 6% to 8% of water The oleostearine may be replaced by a vegetable oil hydrogenated to the approximate consistency of oleostearine

The extent to which margarine simulates the flavor and aroma of butter depends as stated previously upon the manner in which bacterial action is permitted to take place in the milk used in its manufacture Only the best bacterial cultures with proved flavor and aroma producing qualities should be used in ripening the milk As the proper care and maintenance of a culture involves in effect the husbandry of countless successive generations of bacteria it is not a simple matter Apparently quite similar strains of bacteria differ markedly in their ability to produce diacetyl and other substances causing desirable flavors and a culture may lose its good qualities through attenuation or contamination with undesirable organisms The mother culture should be periodically checked for stray organisms by microscopic examination and the ability of the bacteria to produce acetylmethyl carbinol and diacetyl should be confirmed by application of the creatine test[12] or other suitable tests It should be noted that the flavor and odor of the culture or starter itself is a poor indication of its ability to develop diacetyl as prior to emulsification with the fat the tendency is principally toward the production of acetylmethylcarbinol which is relatively flavorless and odorless

In the United States skim milk is almost invariably used for making margarine although in Europe the use of dried milk powders is said to be common The addition of citric acid or citrates to the milk is desirable The milk is first pasteurized to destroy unwanted bacteria and then is ripened by innoculation with the selected butter culture followed by a holding period of 12 to 24 hours at a temperature in the neighborhood of 70°F

The ripened milk and finished margarine fat in the molten form are weighed out in the desired proportions and then are mixed together to form a water in oil emulsion by running the milk into a tank in which the fat is maintained in a state of violent agitation If emulsifying agents are used they are also added at this stage of manufacture

Three different methods are in use for solidifying the emulsion of milk and liquid fat Formerly the most common method of carrying out the solidification process was by continuously pouring or spraying the emulsion

into a trough or vat of cold running water The emulsion entered at one end of the vat, and by the time it had reached the other end it had solidified and floated to the surface of the water in the form of flaky masses, which were then skimmed off This method resulted in both washing out a portion of the milk and occluding portions of the cooling water, so that the moisture content of the solidified product was somewhat uncertain The cooling water was, furthermore, a possible source of bacterial contamination, and was wasteful of refrigeration, since large volumes of water had to be discharged to the sewer without the abstraction of more than a minor part of the refrigeration supplied to it

The various shortcomings of the refrigerated water system led to the widespread adoption in later years of the chill roll for solidifying margarine The application of the roll to margarine solidification is not essentially different from its application to the solidification of shortening, the emulsion is chilled by contact with the exterior surface of a revolving, internally refrigerated drum The disadvantages of the roll are the same in the case of both products, i e, the chilling surface and the product are both exposed to the atmosphere Thus there is opportunity for air borne contamination of the product, and a considerable amount of refrigeration is lost to the surrounding air

In recent years, there has been a pronounced trend toward the "Votator" system of solidification (see pages 706–708), for margarine as well as for shortenings In the Votator, solidification is carried out in a completely enclosed system, with highly efficient utilization of the refrigeration and complete control of the ingredients and product

In plants employing either the cold water or roll method of solidification, it is customary to transfer the solidified emulsion to trucks and hold these for a considerable period of time (24 to 48 hours) in a tempering room at a relatively low temperature before further processing the material This holding period serves to bring the fat to the proper consistency for working and printing, and also allows opportunity for further bacterial action to take place before the product is salted

The incorporation of 2 5% to 3 0% of salt on the basis of the whole product actually raises the salt concentration on the basis of the water content alone to about 20% Consequently, the salting operation effectively terminates the action of the bacteria which are responsible for the development of flavor and odor in the product It is desirable to permit a certain amount of such action after the milk has been mixed with the fat, as the maximum flavor is not developed until after the milk has come into contact with the fat

After the tempering period, the product is passed through working or blending machines which are varied in design These machines break up any aggregates of material in the solidified emulsion, and knead and blend

the fat into a homogeneous mass. In the case of margarine solidified by cold water, the working operation, like the corresponding operation in butter manufacture, results in kneading out any excess of water in the emulsion. The salt is also blended in at this stage of processing The salt used is a special grade manufactured for dairy use, in which the crystals are extremely small. Coarse salt is difficult to dissolve completely.

After the margarine has been salted and worked, there remains but the operation of forming it into prints and wrapping and packaging the individual prints. The forming is most commonly performed by special automatic print formers which take the blended mass, form it into prints of the desired shape and size, and discharge the prints onto a moving belt. The blocks are mechanically wrapped in parchment wrappers and enclosed in cardboard packages. A small envelope of powdered, oil-soluble yellow dye, sufficient in amount to color the print the proper shade of yellow, is

TABLE 104
MARGARINE INGREDIENTS USED IN THE U S. IN 1942

Ingredient	Thousand pounds	Per cent
Fats and oils	346,364	79.4
Milk	74,875	17 2
Salt	13,931	2.98
Derivatives of glycerine (including monostearine).	1,010	0 231
Lecithin	278	0.064
Sodium benzoate	215	0 049
Vitamin concentrates	88	0 020
Miscellaneous	65	0 015

attached to the parchment wrapper or wrappers. The use of workers, blenders, etc., is avoided in the Votator process; the Votator receives the fatty and aqueous ingredients, emulsifies the two, solidifies the emulsion, and forms the solidified prints, in one continuous operation.

Considerable care must be exercised, particularly in the packaging operation, to avoid contaminating the product with molds, many of which will grow freely on the surface of even strongly salted margarine. It is possible to buy wrappers which are, for all practical purposes, sterile; but they may be easily contaminated by careless handling. The best margarine plants are air conditioned, with filtered air, to guard against the possibility of airborne mold contamination.

In addition to the materials mentioned previously, the ingredients commonly used in margarine include sodium benzoate, which is in some cases added to the aqueous phase as a preservative, and vitamin concentrates (chiefly vitamin A) which are added to the fat to improve its nutritive qualities The degree to which the various minor ingredients of margarine are used in the United States is indicated in Table 104, covering the materials reported by the Bureau of Internal Revenue during the calendar year 1942. It will be seen that the use of all of the minor ingredients is

relatively light, inasmuch as the addition of either lecithin or glycerine derivatives is permitted in amounts up to 0 5%, and the permissible and usual addition of sodium benzoate is 0 1%

(i) *Deterioration*

Margarine is subject to a number of varieties of deterioration As in the case of butter, true oxidative rancidity in margarine is probably rare although an objectionable degree of flavor reversion may sometimes occur The margarine fat which is perhaps most likely to develop to a serious degree off flavors from oxidation is oleo oil Hydrogenated soybean oil exhibits the same slight degree of flavor reversion in margarine as in shortenings, even though the margarine may be kept under strict refrigeration So called "soapiness" in margarine is peculiar to nut margarines with a considerable content of acids of low molecular weight It is caused by hydrolysis of the fat through the action of lipolytic enzymes developed from bacterial contamination Free fatty acids of 16 to 18 carbon atoms are not sufficiently soluble to have a noticeable taste, but the acids of low molecular weight of coconut oil are quite objectionable in concentrations of 2–3% or more

Margarines which contain as much as 3% of salt and are stored under refrigeration are unlikely to spoil through bacterial action, even in the absence of sodium benzoate or other preservative Margarine which is to be held without refrigeration should contain a preservative The appearance of mold growth on the surface of margarine is not uncommon, this fault may usually be traced to carelessness in handling the prints or the parchment wrappers

CHAPTER XI

BAKERY PRODUCTS AND CONFECTIONS

1. Introduction

A large part of the total production of lard, shortening, and certain other plastic fats is consumed in the manufacture of commercial baked goods. The average percentages of fat in some of the more popular bakery products are approximately as follows: pie crust, 35–50, pound cake, 15–30, doughnuts, 15–20, cookies and wafers, 5–20, white and yellow layer cakes, 12, soda crackers, 8, pretzels, 5, and white bread, 3.

In 1939 the total consumption of fat products in commercial baked goods in the United States was 765, 750, 584 pounds[1] (Table 106). In point of dollar value, the fats comprised 16.8% of the total raw materials used. The total value of the finished baked products amounted (Table 105) to over $2,000,000,000.

In most classes of baked goods, fat is a highly necessary ingredient, not only because of its contribution to the flavor of the product but also because it plays an essential role in the development of the physical structure. Such important considerations as the volume, the texture, and the tenderness of the finished goods are all closely related to the amount of fat used in the formula, the methods employed in incorporating it and the inherent characteristics of the fat itself.

There are considerable differences in the manner in which different kinds of fat behave in the manufacture of specific classes of baked goods. In some cases these differences are not extreme, and may in fact be so slight as to pass unnoticed in ordinary household use of the fats. In the highly competitive business of commercial baking, however, even minor differences may lead to pronounced discrimination between different fats with the establishment of corresponding differentials in the prices prevailing for the fats.

It is highly desirable for baking fats to be uniform in quality, as an occasional batch of inferior goods may damage a baker's reputation out of all proportion to the actual amount of merchandise involved. Consequently, manufacturers of the better grades of fat products exert every effort to produce materials which are invariable in all important characteristics.

[1] U. S. Bur. Census. *Census of Manufactures*, 1939.

2. Structural Considerations

(a) *Structure of Baked Products*

If bread, cake, pastries, etc , are closely examined, it will be seen that they are more or less cellular in form, and contain a large proportion of voids The adequate development of this cellular structure leads to the lightness and tenderness which is generally associated with good baked products The importance of good structure is particularly evident in the manufacture of cakes The difference between light, well formed cakes

TABLE 105
PRODUCTION OF BAKED GOODS IN COMMERCIAL BAKERIES IN THE U S IN 1939[a]

Baked goods	Production lbs	Value dollars
Bread and other yeast raised products	10,480,950,293	797,294,007
White pan bread	7,218,843,271	491,520 741
Whole wheat, rye and hearth	1,731,225,028	128,210,418
Variety or specialty	462,580,364	37,427,771
Rolls or coffee cake	1,068,301,630	140,135,167
Crackers, biscuit (except raised), sponge goods, sweet goods, machine made cookies	1,611,558,354	207,692,680
Pretzels	52,331,396	6,062,438
Soft cakes		
All types of cake	953,194,658	186,131,250
Cookies, hand made	111,986,405	19,716,112
Doughnuts crullers, other fried cakes	336,018,613	55,374,860
Pies	—	75,121,037
Pastries (French and Danish), cream puffs	—	24,345,898

[a] U S Bur Census, *Census of Manufactures*, 1939

TABLE 106
PRINCIPAL MATERIALS CONSUMED IN THE MANUFACTURE OF BAKED GOODS IN COMMERCIAL BAKERIES IN THE U S IN 1939[a]

Material	Quantity	Value dollars
Flour	46,984,034 bbls	215,618,942
Sugar	1,256,012,386 lbs	58,948,204
Eggs	—	33,897,687
Butter	39,181,843 lbs	10,802,028
Oleomargarine	31,017,544 lbs	3,446,082
Lard	284,171,707 lbs	22,443,843
Shortenings	411,379,490 lbs	40,581,315
Milk (fluid, condensed, evaporated, powdered)	476,204,974 lbs	27,807,957
Malt extract	40,175,756 lbs	2,913,022
Fruit	—	21,970,746
Yeast	147,770,275 lbs	20,642,179
Salt	189,205,224 lbs	1,854,337

[a] U S Bur Census, *Census of Manufactures*, 1939

and those which are complete failures usually lies solely in the relative proportions of solid materials and voids in the two

Good volume in breads, cakes and similar products is considered particularly essential by the commercial baker This is true not only because good volume is associated with good texture and other desirable properties, but also because the purchaser is inclined to judge the baker's offerings by their apparent size rather than by their weight

The size of the individual cells is also a matter of some importance, as fine and even grained products are superior in appearance and texture to those which are coarse and irregular in grain Thus the volume of baked products cannot well be developed at the expense of grain and texture The fineness or coarseness of grain depends upon the average size of the cells The evenness of grain depends upon their size distribution

The cellular structure of baked products is produced by the expansion of gases within the dough while the latter is still soft and extensible In the following pages the term "leavening" is applied generally to the process of gas generation and expansion, with accompanying increase in volume of the product

From the standpoint of the leavening process, baked goods may be divided into two broad classes, namely those which are leavened with yeast and those which are leavened by other means In the case of yeast raised goods, leavening occurs over a considerable period of time, and is partially effected before the dough enters the oven In most doughs which are leavened without the use of yeast leavening is much more rapid, and occurs principally after the dough is subjected to the heat of the oven

In bread and other yeast leavened products, a fairly satisfactory cellular structure may be produced without fat being present There are also a few non yeast raised products such as sponge cakes, in which fat does not play an essential role in the leavening process Other types of cakes however, and many other products, require a considerable proportion of fat for the development of their characteristic structure

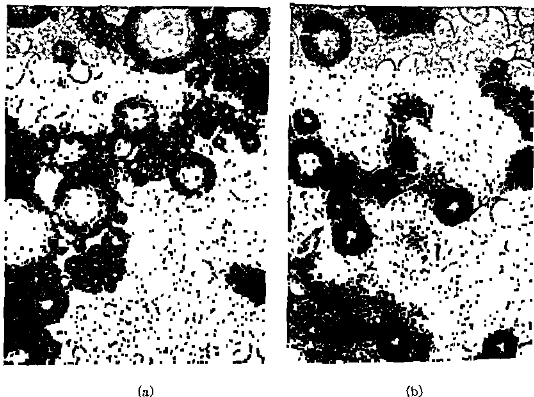
A second important function of the fats used in baking is one of lubrication If a finished baked product of the cake type is subjected to microscopic examination, it will be seen that the solid material comprising it is not homogeneous The continuity of the gluten and starch structure comprising the cell walls is broken by films of fat These weaken the structure of the product sufficiently to make it tender and easily disintegrated when it is eaten

Certain baked products, such as pie crust and certain pastries and cookies, are formed from a stiff dough rolled into a thin sheet The rolling process has the effect of spreading the incorporated fat into thin, parallel layers In the finished products the natural lines of cleavage are along the fat layers, thus a "flaky" structure is produced All cookies, biscuits, wafers, etc, which are baked in a thin form from a dough low in moisture, require a

large percentage of fat, to prevent the relatively dry gluten and starch from compacting into a hard, refractory mass.

(b) Relation of Fat to the Leavening Process

Although fat plays an important role in the leavening of other products, its peculiar action is best exemplified in the manufacture of ordinary yellow cakes. Cake doughs consist of certain dry, or nonaqueous ingredients: flour, sugar, salt, baking powder, fat, etc., mixed with other watery or liquid



(a) (b)

FIG 28 —Photomicrographs (× 290) of pound cake dough with (a) good incorporation of air and (b) poor incorporation of air

ingredients: egg and milk. In the process of mixing, the sugar, baking powder, and salt dissolves in the liquid ingredients.

The resulting solution mixes freely with the particles of flour, but not with the fat. Thus the dough is in effect a two-phase system. The two phases consist, respectively, of the fat, and all the other ingredients of the mixture.

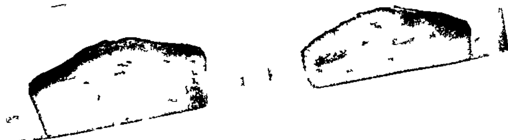
If a small amount of an

tion, to stain the fat, and

fat will be seen to be dispersed throughout the dough in the form of small, irregularly shaped particles (Fig. 28). Within each particle of fat there will be enclosed numerous small bubbles of air, incorporated during the

mixing operation No air will be entrapped in the aqueous phase of the dough

The examination of numerous different samples of dough will reveal that the latter exhibit some variation with respect to the size of the fat particles and the amount of incorporated air If the doughs are baked into test cakes it will be found that there is a close correlation between the volume and other qualities of the finished cakes and the structure of the doughs from which they are baked The doughs containing large amounts of air entrapped within the fat will produce cakes larger in volume than will those containing relatively little air And cakes made from doughs in which the entrapped air is well dispersed will have a finer grain and texture than those in which it is not well distributed They will also be less inclined to fall or collapse while they are being baked



(a) (b)

Fig [illegible] Cakes from pound cake doughs with (a) good incorporation of air and (b) poor incorporation of air (cf Fig 28)

The exact mechanics of the leavening process are to some extent a matter of conjecture However certain facts may be deduced from relations observed between the structure of doughs and that of the finished products It appears that pockets of gas tend to form at the points where there are particles of fat The development of a gas pocket requires a cleavage of the dough mass and it is reasonable to assume that cleavage will most readily occur along the fat boundaries Probably as a particle of fat melts the air entrapped in it migrates to the water–fat interface and serves as a nucleus for the accumulation of water vapor and carbon dioxide (from the baking powder or other chemical leavening agent) *

* This hypothesis of leavening is confirmed by the recent experiments of G T Carlin (reported before the 29th annual meeting of the American Association of Cereal Chemists St Louis Mo May 17 to 19 1943) in which the action of entrapped air was actually observed and cinemaphotographed under the microscope

It is certain that the air in the fat contributes a leavening action out of proportion to its normal thermal expansion in the oven The experiments in Table 107 illustrate the typical effect of the incorporation of air in a pound cake formula containing 21% of fat and no chemical leavening agent To these may be added the observation by Dunn and White[3] that pound cake doughs wholly devoid of air do not rise at all when baked It is apparent that the thermal expansion of the air is a very minor factor in the leavening process, and that the greater part of the expansion of the dough in the oven is due to the increased vapor pressure of water in the air bubbles at high temperatures Water vapor can not assist in the leavening process unless air is initially present in the dough, and the extent to which it assists is more or less proportional to the amount of air present

TABLE 107
TYPICAL EFFECT OF INCORPORATING AIR IN A POUND CAKE FORMULA CONTAINING 21 PER CENT FAT AND NO CHEMICAL LEAVENING AGENT

Experiment	A	B
'	Low 377	High 377
cc	543	662
Volume of air in dough, cc	166	285
Volume of cake cc	1140	1520
Expansion of dough during baking cc	597	858
Calculated expansion of air due to heating in oven (70–212°F) cc	42	71
Percentage of total expansion due to thermal expansion of air	7 0	8 3
Percentage of total expansion due to increased vapor pressure of water	93 0	91 7

An important feature of the leavening contributed by water vapor in conjunction with air is that it is controlled, *i e*, the expansion of gas takes place at points which are predetermined by the position of the fat-entrapped air bubbles By conducting the mixing operations in such a manner as to cause the fat to enclose much air, and then distributing the fat well through the dough, leavening can be made to take place uniformly through the dough, with the production of a cake of fine and uniform grain and texture

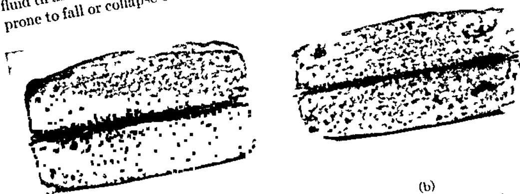
In actual practice most cakes are made with an insufficient quantity of fat to supply the entire amount of leavening desired, hence the action of the air and water vapor must be supplemented by carbon dioxide generated from baking powder or other suitable chemical leavening agent If the leavening supplied by the baking powder is not disproportionate to that obtained from the air and water vapor, a cake of good structure results, as in this case the carbon dioxide appears to merely reinforce the action of the

[3] J A Dunn and J R White *Cereal Chem*, 16, 93–100 (1939)

water vapor If too little air is incorporated in the fat, however, and the deficiency in air is compensated by the use of an excessive amount of baking powder, the cake will be coarse grained, with many large cavities and tunnels, due to the action of the baking powder being uncontrolled by the air

In the manufacture of pound cakes containing no baking powder no particularly good dispersion of the fat is obtained (compare, for example, Figs 28 and 37), but a very fine grained cake is obtained, due to the fact that the leavening action is entirely controlled by the incorporated air

A fine cellular structure is also desirable in cake making because of the mechanical strength which it imparts to the dough The sugar used in cake and other sweet doughs weakens the dough and tends to make it more fluid than unsweetened dough Consequently, cake doughs are particularly prone to fall or collapse of their own weight during that period of the baking



(a) (b)

Fig 30 — Yellow cakes with (a) fairly fine grain and (b) coarse grain

operation just prior to their assuming a "set" form, due to coagulation of the starch and protein in the flour

A soft, partially baked dough of fine cellular structure is much stronger and less likely to collapse than one of coarse structure

(c) *Shortening Values of Different Fats*

The ability of a fat to lubricate and weaken the structure of a baked product is known as its shortening value The relative shortening values of different fats may be determined by means of the "shortometer" This instrument, which was devised by Davis[4] and improved by Bailey[5] measures the breaking strength of standard test biscuits or wafers, which are shortened with the fats under test

[4] C E Davis *Ind Eng Chem*, **13**, 797–799 (1921)
[5] C H Bailey *Cereal Chem*, **11**, 160–163 (1934)

Somewhat discordant results have been obtained by the various investigators who have attempted to evaluate different fats on the basis of their shortening power [6] However, it would appear that the shortening value of a fat is *principally* dependent upon its consistency, soft fats such as prime steam lard being superior in this respect to firmer fats, such as all hydrogenated *shortenings* The superior shortening value commonly attributed to lard may also be related to the characteristically coarse crystal structure of this fat (see pages 213–214)

Platt and Fleming [7] reasoning from the concepts of surface chemistry developed by Harkins, Langmuir, and others, have advanced the theory that the particular effectiveness of lard as a shortening material is due to its relatively high content of unsaturated fatty acids This theory, however, does not appear to be supported by experimental evidence

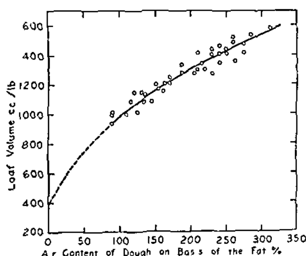


Fig 31 —Air content of pound cake doughs *vs* loaf volume of the finished cake

The inadequacy of liquid oils as shortening agents is undoubtedly due to their lack of plasticity Particles of oil in a dough are drawn into spherical globules by their surface tension (Fig 32) and thus cannot be dispersed in streaks and films through the dough in the manner of plastic fats

(d) *Creaming Quality*

The absorption of air by fats during mixing operations in the bakery is termed ' creaming ' As explained above the creaming ability of a fat is a highly important factor in determining its value as a shortening agent

[6] See for example J D Fisher *Ind Eng Chem* 25 1171 1173 (1933) A W Harvey *ibid* 29, 1155–1159 (1937) and L R Hornstein F B King and F Benedict *Food Research* 8, 1 12 (1943)

[7] W Platt and R S Fleming *Ind Eng Chem* 15 390–394 (1923)

The creaming quality of a fat may be tested or the creaming may be followed through the various stages of preparing a dough by periodically determining the density of the dough or other mixture. The creaming is best expressed as the percentage of air incorporated by the fat on the basis of its own volume.[8] When a test is conducted by simply mixing together fat and sugar, the relative proportions of fat and sugar and the size and shape of the sugar granules influence the amount of air which the fat will absorb. The optimum ratio of sugar to fat for maximum air incorporation is approximately 3 to 2 by weight. The finer the granulation of the sugar the greater is the incorporation of air.[9] Decreasing the particle size by grinding is not effective in promoting increased creaming, however, as the ground particles are less effective in entrapping air than are naturally

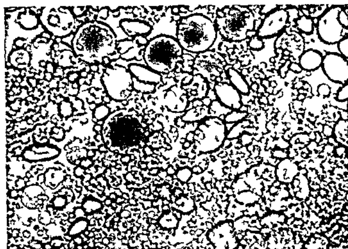


FIG. 32. Photomicrograph (× 300) of pound cake dough made with a liquid oil.

formed crystals. The action of sugar in promoting air absorption appears to be purely mechanical. The presence of any other granular substance will also increase the capacity of fats to take up air.

Different fats differ very markedly in their creaming properties. Typical creaming tests on different fats at 70°F with a 3 to 2 ratio of sugar to fat are shown in Table 108. For fats to cream satisfactorily it appears to be necessary for them to contain certain highly saturated glycerides.[10] Hydrogenation appears to be particularly effective for the production of good

[8] See A. E. Bailey and R. H. McKinney, *Oil & Soap*, **18**, 120–12[illegible] (1941).

[9] J. A. Dunn and J. R. White, *Cereal Chem.*, **14**, 783–801 (1937).

[10] Glycerides of intermediate melting point separated from hydrogenated lard or all hydrogenated shortenings cream very poorly, even though they have the consistency of shortening at the temperature at which the creaming tests are conducted.

creaming fats. Limited hydrogenation of any oil or soft fat will produce a shortening of good creaming quality, as will the addition of a small proportion of highly hydrogenated fat. Lard will not cream well without hydrogenation or the addition of hydrogenated fat. The creaming quality of butter is variable and generally inferior to that of hydrogenated or compounded shortenings. "Untempered" shortenings, *i.e.*, shortenings placed directly under refrigeration after filling, without a tempering period *at about 85°F.*, are notably deficient in creaming quality.

When cakes are mixed by the common "sugar batter" method, wherein the shortening is mixed first with the sugar, then with the eggs, and last of all with the milk and flour, the fat is not ordinarily creamed to its maximum

TABLE 108

CREAMING TESTS OF VARIOUS FATS AT 70°F.[a] (AIR INCORPORATION CALCULATED BY VOLUME, ON THE BASIS OF THE FAT)

Fat	Iodine value	Per cent air incorporated after mixing for specified times (min.)						
		4	8	12	16	20	24	28
All hydrogenated vegetable shortening	62	165	215	240	265	275	280	280
Compound type shortening "A"[b]	90	190	240	270	280	280	280	280
Compound type shortening "B"[c]	73	150	195	230	255	270	275	275
Prime steam lard	69	85	125	145	150	155	155	155
Prime steam lard with 8% hydrogenated lard stearine added	65	155	205	235	260	270	275	275
Hydrogenated prime steam lard	61	150	200	240	260	270	275	280
All hydrogenated vegetable shortening, untempered	62	120	160	175	180	185	185	185

[a] 1.0 lb. fat mixed with 1.5 lbs. fine granulated fruit sugar at medium speed in Hobart bench mixer with 12 qt. bowl.

[b] Compounded from slightly hydrogenated cottonseed oil and hydrogenated cottonseed oil stearine.

[c] Compounded from vegetable stearine, slightly hydrogenated cottonseed oil, and tallow.

air content in the first stage of mixing. The usual practice is to first cream the shortening and sugar to an air content of 150–200% on the basis of the fat, and then add the eggs. The presence of the eggs increases the capacity of the shortening to hold air; after their addition to the mix, the air content of the fat may usually be increased to 275–325%.

Hydrogenated lard incorporates air well when creamed with sugar, but has the peculiarity of often losing rather than gaining air when eggs are mixed into the fat–sugar mass. Typical pound cake baking tests on lards and hydrogenated lard, in comparison with all hydrogenated vegetable shortening, are shown in Table 109.

Concurrently with the loss of air in the mixing process, the emulsion of hydrogenated lard, eggs, and dissolved sugar becomes very thin and sloppy. Microscopic examination of the emulsion will reveal that it presents the

appearance of being broken, and partially inverted from the smooth water-in oil structure characteristic of that produced by other shortenings (see Fig 33)

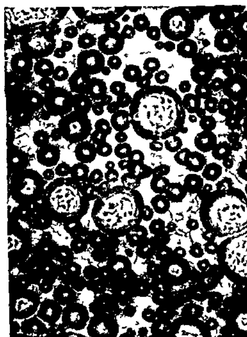
TABLE 109

POUND CAKE BAKING TESTS ON LARD AND OTHER SHORTENINGS[a]

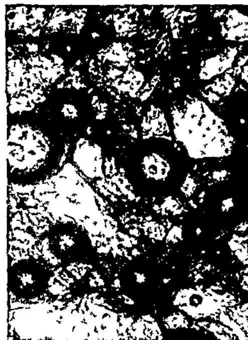
Fat used	Temp of test °F	Per cent air in fat at end of mixing period indicated[b]				Loaf volume cc /lb
		1	2	3	4	
Prime steam lard	70	100	120	98	78	995
Prime steam lard + 8% hydrogenated stearine	70	140	152	130	102	1040
Leaf lard	80	62	88	80	72	895
Hydrogenated lard	70	211	172	166	117	1085
All hydrogenated vegetable shortening	70	170	265	300	270	1475

[a] Formula of pound cake, parts by weight fat, 88, sugar, 100, eggs, 112, milk, 12, flour 100

[b] Mixing period 1 refers to that (5 min) during which the fat and sugar are mixed, during period 2 (5 min) the eggs are gradually added, during period 3 (5 min) mixing of fat sugar and eggs is continued, during period 4 (3 min) the milk and flour are added



(a)



(b)

FIG 33 —Pound cake batters (fat sugar, and eggs) (a) normal, unbroken emulsion and (b) emulsion broken from secondary crystallization (× 200)

The breaking of the emulsion, with accompanying loss of air, is possibly caused by a secondary formation of fat crystals, which occurs when the temperature of the mix drops, due to the negative heat of solution of the

sugar in the eggs. It can be prevented by applying heat to the mixing bowl during the period that the eggs are added and it does not occur in the manufacture of cakes by the 'flour batter' method (page 298) in which the sugar is dissolved in the eggs before they are added to the fat and flour.

The harmful effect of secondary crystallization in lard products appears to be associated with the characteristically coarse crystal structure of these fats (see pages 213–214 section on plastic shortening agents). Vegetable shortenings which are slowly solidified to produce coarse crystals lose air in the mixing process in a manner similar to lard and rearranged lard which has had its molecular structure altered to cause it to form small crystals (see pages 681–682) is not subject to loss of air. Typical pound cake tests illustrating the preceding statements are recorded in Table 110.

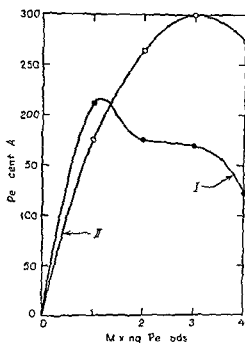


Fig. 34.—Typical curves illustrating the incorporation of air during the mixing of pound cakes. I hydrogenated lard. II hydrogenated cottonseed oil.

The maximum amount of air which a fat is capable of incorporating does not vary a great deal over a considerable temperature range although within their effective creaming range fats will cream more rapidly when soft than when relatively firm. Manufacturers naturally endeavor to produce shortenings which have optimum properties at ordinary mixing temperatures. The recommended working range for all hydrogenated shortenings is 70° to 80°F although most products will mix and cream satisfactorily at temperatures 10° outside of this range on either the high or the low side. Compound type shortenings will cream well over a wider temperature range than all hydrogenated products.

(e) Emulsification and Dispersion

As stated previously a dough is actually an emulsion in which the internal phase is the fat and the external phase is comprised of the remaining ingredients. Since the fat is plastic rather than liquid the oily phase consists of irregularly shaped particles rather than spherical globules. Thus the fat particles cannot actually coalesce as in an ordinary oil in water emulsion. However they may agglomerate into large masses and in general the problems involved in producing a good emulsion in a dough are analogous to those encountered in producing emulsions of liquid oil in an aqueous medium.

One of the functions of the eggs used in cakes is to serve as an emulsifying agent, to promote dispersion of the fat. Lately, however, shortenings have

TABLE 110

POUND CAKE BAKING TESTS WITH LARD PRODUCTS AND OTHER SHORTENINGS USING DIFFERENT METHODS OF MIXING[a]

Fat used	Method of mixing	Temp. of mix, °F			Per cent air in fat at end of mixing period indicated[b]				Loaf volume, cc./lb.
		Initial	Max.	Final	1	2	3	4	
Hydrogenated lard	Sugar batter, regular mixing method	70	76	68	170	184	172	150	1140
Hydrogenated lard	Sugar batter iso thermal mixing method[c]	70	80	80	158	270	288	262	1520
All hydrogenated shortening	Sugar batter, regular method	70	77	69	165	265	290	270	1510
All hydrogenated shortening (coarsely crystallized)	Sugar batter regular method	70	76	69	182	97	85	88	995
Hydrogenated lard	Flour batter	70	—	—	—	—	—	230	1250
All hydrogenated shortening	Flour batter	70	—	—	—	—	—	223	1200

[a] Formula of cake parts by weight fat 88 sugar 100 eggs, 112, milk 12, flour, 100

[b] [illegible] (5 min) eggs gradually mixed [illegible] continued, period 4 (3 min)

[c] [illegible] drop in temperature

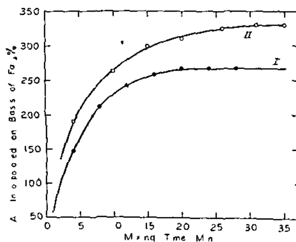
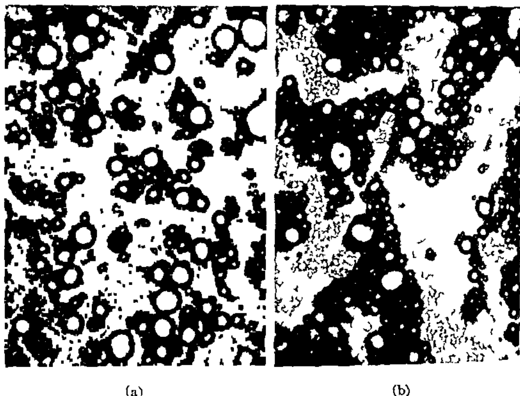


FIG 35.—Typical creaming tests of shortening with good creaming properties I 40% fat-60% sugar, by weight II, 30% fat 33% sugar-37% eggs by weight

been introduced which contain more powerful synthetic emulsifying agents These so called "superglycerinated" shortenings (see pages 244–245), contain mono and diglycerides which are extremely effective in promoting and stabilizing emulsions of both the water in oil and oil in water types

While the effectiveness of mono and diglycerides in cake doughs is explainable in terms of conventional theories of emulsification, on the basis of their content of hydrophilic (hydroxyl) and lipophilic (fatty acid) groups, it is nevertheless somewhat surprising that they are so much more efficient than a number of other emulsifying agents. There are other edible emulsifiers, such as soybean lecithin, which are very effective in lowering the interfacial tension of fat against water, but none of these are capable of conferring satisfactory emulsifying properties upon baking fats.



(a) (b)

FIG 36.—High ratio yellow cake doughs made with (a) superglycerinated and (b) ordinary all hydrogenated shortening (× 72)

The principles involved in the use of superglycerinated shortenings have been discussed at some length in a preceding chapter. As mentioned previously, the difficulty of maintaining the fat in sweet dough in a highly dispersed condition increases with increasing water and sugar content of the dough. With ordinary fats it is not possible to produce a good cake dough if the combined amount of milk and sugar in the formula amounts to more than about 40% to 45% of the total ingredients. With the use of high ratio shortenings it is possible to increase the milk and sugar to as much as 50% to 55% of the total. The difference between ordinary fats and superglycerinated fats, with respect to their dispersion in high sugar and liquid content doughs, is shown in the photomicrographs of Figure 36.

Since shortening, lard, and similar fats are plastic products with a more or less rigid structure, they are capable of absorbing and holding considerable quantities of water without benefit of an emulsifying agent The extent to which a fat is capable of taking up water may be determined by slowly mixing water into the fat in a small baker's mixing machine For some reason hydrogenation improves the ability of a fat to emulsify water Lard and compound type shortenings consisting principally of unhydrogenated oil will usually absorb 25% to 50% of water at 70°F whereas hydrogenated lard will absorb 75% to 100% and all hydrogenated vegetable shortenings will take up 150% to 200% High ratio shortenings will emulsify 400% or more of their own weight of water assuming in the process an elastic gel like structure

From a practical standpoint, the variations in water absorbing capacities of different fats do not appear to be as significant as might be supposed When compound type shortenings of low emulsifying capacity and non superglycerinated all hydrogenated shortenings of high emulsifying capacity are mixed with eggs in the actual manufacture of cake or other sweet doughs there is no apparent difference in either the water in oil emulsions of sugar fat and eggs, or the oil in water emulsions of the finished doughs

3 Nonstructural Considerations

(a) *Stability of Fats in Baked Goods*

A large volume of baked goods consists of products such as soda crackers and various sweet biscuits which are normally packaged and held for considerable periods of time before they are consumed As these products are not packed in containers which protect the contents from the air, the fat used in their manufacture may in time become rancid

The matter of fat stability in baked goods has not been extensively investigated However, the few investigations which have been reported have emphasized that the problem is considerably different from that of the stability of fats in their original form The difference observed between the deterioration of pure fats and the same fats in baked goods is probably associated with both the heat treatment accorded the fat in the baking process and the presence of materials in the flour and other ingredients of the mixture which influence the oxidation of the fat

Various investigators have observed a lack of correlation between the keeping qualities of different fats and the stability of crackers and other products made from the same fats Triebold, Webb, and Rudy[11] found that in some cases lards which were on the verge of rancidity produced crackers of better keeping quality than did lards of good stability Bohn and Olson[12] prepared soda crackers from different fats, and observed that

[11] H D Triebold R E Webb and W J Rudy *Cereal Chem* 10 263–276 (1933)

the stability of the crackers decreased, not with the stability of the fats, but with increase in the degree of unsaturation of the fats. They attributed this effect to the destruction of antioxidants in baking which would of course make the stability of the fat entirely dependent upon its fatty acid composition. They found that commercial crackers made with corn oil became rancid almost immediately at 145°F but that crackers made with lard would withstand accelerated oxidation at this temperature for 2 to 6 days. They also found that crackers made with oleo oil would keep under the same conditions for 6 to 15 days, and that crackers made with all hydrogenated vegetable shortenings of the biscuit and cracker type would keep as long as 40 days. The stabilities of corn oil, lard, oleo oil and all-hydrogenated shortenings of this type as measured by the Swift accelerated method, were of the order of 10, 8, 12, and 120 hours, respectively.

The conclusions of Bohn and Olson were confirmed in some respects by McKinney and Bailey[13] who found biscuits made with hydrogenated lard to be virtually as stable as those prepared from hydrogenated vegetable oil. That lard is very low in its content of natural antioxidants in comparison with vegetable oils, is well known. It is known that antioxidants, of the acidic type, including lecithin, are inactivated by the baking process[1, 13] although the destruction of tocopherols or other phenolic antioxidants in baking has not as yet been specifically noted.

Sugar serves as an antioxidant for the fat in baked goods in which it is incorporated. Hence sweet cookies and biscuits present a much less acute problem from the standpoint of deterioration than do soda crackers and other unsweetened products. The antioxidant effect of sugar appears to be somewhat less in baked products made from lard than in those made from other fats including hydrogenated lard. The influence of sugar on the stability of fats in baked goods is illustrated by the data of Table III which shows the effect of adding 160% of sugar, on the basis of the fat, to a simple unleavened biscuit formula.

Soda crackers, according to Bohn and Olson,[1] are extraordinarily susceptible to metallic contamination, and are considerably injured in keeping quality by being mixed in commercial steel equipment. Crackers mixed in glass in the laboratory and subjected to accelerated oxidation at 145°F were found to be markedly superior in keeping quality to crackers containing the same fats but mixed in the factory. In some cases even the use of a metal cutter on cracker doughs otherwise unexposed to metal surfaces decreased the stability of the crackers by as much as 50%.

The reason for the relatively poor performance of sugar as an antioxidant

[13] R. H. McKinney and A. E. Bailey, *Oil & Soap* 18, 147-148 (1941).

in baked products containing lard is by no means clear[14] It might reasonably be supposed that sugar acts synergistically with tocopherols or other substances which are not present in lard However, this does not explain the effectiveness of sugar when used with hydrogenated lard

TABLE 111

STABILITIES OF VARIOUS FATS AND BISCUITS MADE THEREFROM (WITH AND WITHOUT SUGAR)[a]

Fat	Stability of fats		Stability of biscuits: Days to become rancid at 98°F	
	Swift method hrs at 210°F	Schaal method days at 145°F	Without sugar	With sugar
Prime steam lard	8	10	34	50
Oleo oil	10	12	50	320
Hydrogenated lard (I V = 60 3)	22	26	75	360
Hydrogenated vegetable oil (I V = 58 3)	70	70	80	360

[a] R H McKinney and A E Bailey, *Oil & Soap*, **18**, 147–148 (1941)

TABLE 112

COMPARATIVE STABILITIES OF DIFFERENT FATS IN BISCUITS STORED AT 98° AND 120°F[a]

Fat	Kind of biscuit	Days for biscuits to develop rancidity: At 120°F	At 98°F
Prime steam lard	Unsweetened	3	34
	Sweetened	11	50
Oleo Oil	Unsweetened	5	50
	Sweetened	37	320
Hydrogenated lard	Unsweetened	7	75
	Sweetened	22	360
Hydrogenated vegetable oil	Unsweetened	16	80
	Sweetened	55	360

[a] R H McKinney and A E Bailey, *Oil & Soap*, **18**, 147–148 (1941)

The validity of heat-accelerated stability tests on baked products has been questioned by McKinney and Bailey[13] inasmuch as they found that an increase in the storage temperature from 98° to 120°F did not have a uniformly accelerating effect on the oxidation of different fats in sweetened and unsweetened biscuits (Table 112)

[14] It is to be noted that other workers have in some cases observed a relatively higher stability in sweetened biscuits made with lard than that reported by McKinney and Bailey Thus for example, G T Carlin (private communication) reports a 3 3 to 1 ratio between the stabilities of sweetened and unsweetened lard biscuits at 98°F

(b) *Behavior of Fats in Commercial Deep Frying*

Large quantities of oils and fats are used in the commercial frying of s products as doughnuts, potato chips, nuts, etc , as well as in the prepara of a variety of fried foods in restaurants and hotels

Commercial frying differs from that practiced in the household in t the products to be cooked are invariably "deep fried," by immersion i large body of fat, rather than being merely sautéed Also, the large qu tities of material passed through the fat make a constant replenishmen it necessary Consequently, the contents of the frying kettle are incl to consist of an equilibrium mixture of fresh fat with fat which has un gone an indefinite period of use

For products which are fried in large quantities, such as doughnuts, frying kettles are usually equipped with thermostatic controls, which ma tain the fat at a constant temperature, and with fully automatic machine which continuously feeds the raw food into the kettle and withdraws a drains it after a predetermined cooking period

The temperature employed in deep frying varies from about 325–350° in the frying of nuts or potato chips, to about 390°F in doughnut fryi At these temperatures fats hydrolyze appreciably in the presence of wat As all of the foods which are commonly fried are more or less wet, fats us for frying exhibit a progressive increase in their content of free fatty aci Some polymerization also takes place during the frying operation, as evidenced by a gradual accumulation of gummy material on the botto or edge of the frying kettle

Since frying is always conducted with the surface of the fat freely expos to the air, it might be supposed that the fat would rather quickly becor rancid while in use Such, however, is not the case While the exposu of fat to oxygen at high temperatures will certainly impair its stability, does not appear that fat is capable of actually becoming rancid while is very hot The high temperatures prevailing in the frying kettle preve the formation of peroxides, and apparently otherwise break up the reactio leading to the development of true rancidity Also the continual vaporiza tion of water from the surface of the frying food provides a kind of contin ous steam distillation, which seems to remove volatile substances from t fat, and probably contributes to maintaining it in a nonrancid and rel tively flavorless and odorless condition For frying potato chips, nuts, an other foods which are packaged and not immediately consumed, relative stable fats, such as coconut oil and all hydrogenated vegetable shortenin are preferred For doughnut frying, however, and for general use restaurants and hotels, fats of ordinary stability, such as compound typ shortenings and cooking oils, are satisfactory

When a fat is heated to a high temperature, *its tendency to smoke is direct proportion to its content of free fatty acids* At a frying temperatu 390°F , smoking will occur if the fat contains more than about 0 1%

free acids Although the shortenings and cooking oils of the highest grade are manufactured with free fatty acids not exceeding 0 03%, this low initial acid content is not maintained with even slight use of the fat Most commercial deep frying is actually conducted in fat containing 1% or more of free acids Consequently, all fats can be expected to smoke considerably in commercial use Obviously, minor differences in the initial smoke points of different fats are of little practical significance

Very extensive deep frying tests, involving the use of commercial doughnut machines and the preparation of nearly 200 000 doughnuts have been reported by Lantz and Carlin [15] Five different shortenings were used in the tests, three of the shortenings were of the all hydrogenated variety, and

TABLE 113

DOUGHNUT FRYING TEST[a] WITH ALL HYDROGENATED VEGETABLE OIL SHORTENING (IODINE VALUE = APPROXIMATELY 62)

Days	Frying time hrs min		Doughnuts fried total no	Fat		
	Daily	Cumulative		FFA %	Peroxide value[b]	Flavor and odor
0	0	0	0	0 02	2	Good
1	2 20	2 20	46	0 07	7	Good
2	2 00	4 20	91	0 11	7	Good
3	2 00	6 20	132	0 18	8	Good
4	2 10	8 30	174	0 25	8	Good
5	2 00	10 30	228	0 32	9	Good
6	2 05	12 35	283	0 47	9	Good
7	2 00	14 35	341	0 60	5	Good
8	2 00	16 35	394	0 70	5	Good
9	2 40	19 15	447	0 95	5	Good
10	3 00	22 15	507	1 10	5	Good
11	2 45	25 00	559	1 23	5	Good

[a] 15 pounds of fat 14 inch kettle at 385°F

[b] Milliequivalents per 1000 grams fat

two were of the compound type and contained about 80% of unhydrogenated cottonseed oil The machines were operated continuously 14 hours a day, for a total frying time of 100 hours Fresh fat was added hourly to replenish that absorbed by the doughnuts Under the condition of the test, the different fats reached in about 80 hours an equilibrium free fatty acid content varying from 0 70% to 1 35% All of the fats darkened greatly during the test, their Lovibond red colors increasing from 1 5–3 5 units to 20–30 units There was no correlation between the original colors of the fats and their final colors The compound type shortenings, as a group, exhibited no greater tendency to develop free fatty acids than the all hydrogenated shortenings, although they were slightly more inclined to form gum It was concluded that compound type shortenings are not significantly less satisfactory for deep frying than the more expensive all hydrogenated products

The data recorded in Table 113 are typical of small scale doughnut frying

[15] C W Lantz and G T Carlin, *Oil & Soap* **15**, 38–41 (1938)

tests in which no fat is added to the kettle during the course of the test In this test an initial charge of 15 pounds of fat was used for frying on 11 successive days The frying period during each day was approximately 2 hours, and the fat was allowed to cool after each day's use

With prolonged use, frying fats are inclined to foam This is probably due to solution or colloidal dispersion in the oil of surface active substances derived from the fried food Fats containing large proportions of coconut oil, or other oils with fatty acids of low molecular weight, foam very readily and consequently are not very suitable for frying foods of high moisture content

4. The Different Classes of Baked Goods

(a) Bread

Bread is one of the lowest of all baked products in fat content The average amount of fat included in bread dough is between 2% and 3% athough it has been claimed[16,17] that the quality of bread is improved by increasing its fat content to 4% or even 6% A typical formula for white bread is as follows (in parts)

Flour	55 0
Milk	37 5
Shortening	3 0
Sugar	2 0
Yeast	1 5
Salt	1 0
TOTAL	100 0

Unlike most other baked products, bread does not absolutely require fat in its composition A reasonably good bread can be made without the assistance of any fat other than the small amount of wheat oil present in the flour, and French bread and hard rolls are often so made However, the use of a small quantity of shortening not only increases the volume of the bread loaf, but also yields a sponge which is more easily broken up, as well as a smoother dough, and a bread with a more tender crumb[18]

Baker and Mize[19] have noted the action of shortening materials in bread in connection with an investigation of the changes occurring in bread dough during the process of baking In the course of baking they found that the dough began to become strengthened at a temperature of 136°F because of "starch swelling" The swelling abstracts water from the gluten in the dough and makes it both stronger and more elastic The final strengthening of the dough is due, of course to coagulation of the gluten, which begins at 165°F There is a critical period between about 100° and 136°F, however, when the dough is very soft, and apparently more or less permeable

[16] G F Garnatz Oil & Soap, 12, 290–293 (1935)
[17] W L Heald Cereal Chem 16, 817 820 (1939)
[18] B Sullivan Cereal Chem 17, 666–667 (1940)
[19] J C Baker and M D Mize Cereal Chem, 16, 682–695 (1939)

to gases Bread made without shortening or bread shortened with liquid oils was observed to be deficient in volume because of its failure to retain leavening gases during this critical softening period The unshortened or oil-shortened loaves were of good texture and a good cell structure there was no evidence of the loss of gas being due to rupture of the cells It was concluded therefore that plastic fats gave loaves of high volume due to their being able in some way to inhibit the diffusion of gas through the cell walls

Probably the mechanisms mentioned previously in connection with cake leavening apply also in some degree to the leavening of bread In other words cleavage of the dough to form gas filled cells probably is inclined to take place at places where the continuity of the dough is broken by layers of fat This would tend to leave the cell walls coated with films of fat which would undoubtedly decrease their porosity Liquid oils do not form fat layers or films in the dough but are formed into spherical globules by forces of surface tension (see Fig 32 page 281) which become very powerful as the fat is finely dispersed

Although various plastic fats are used for shortening bread the material which probably enjoys the widest use is lard Many bakers consider that it contributes in a desirable way to the flavor of the product Lard also has the advantage of being relatively soft and easily handled Most of the bread which is not shortened with lard is made with compound or all hydrogenated shortenings

Appreciable quantities of fat are used in commercial bakeries for greasing bread pans As the pans are but infrequently washed this particular service requires a fat which is not only easily applied but is also not inclined to become gummy with long continued use The preferred fat for the purpose is lard oil prepared by removing the higher melting portions of ordinary lard by means of fractional crystallization

(b) Yeast Raised Sweet Goods

A variety of buns rolls coffee cakes etc are made from a yeast leavened sweet dough containing 10% or more of sugar Such sweet doughs require considerably more shortening in their preparation than do ordinary bread doughs The average content of fat in yeast raised sweet doughs is perhaps 10% The following is a typical formula for this variety of dough (in parts)

Flour	47 0
Milk	21 0
Shortening	10 0
Sugar	10 0
Whole eggs	7 5
Yeast	4 0
Salt	0 5
TOTAL	100 0

The shortening agents used in the manufacture of this class of goods include, lard, butter, and compound and all-hydrogenated shortenings. The creaming qualities of the fat are not as important in this application as they are in making cakes, but the flavor is of some importance, and it is important that the fat be plastic and capable of being well dispersed in the dough. Superglycerinated shortenings, because of their ability to become highly dispersed, are claimed to produce sweet yeast goods of superior texture and tenderness. The use of shortening materials containing mono and diglycerides in this class of products is patented.[20]

(c) Soda Crackers

Soda crackers usually contain from 7% to 10% of fat, which is necessary to impart to the product its characteristic flaky structure. The following is a typical soda cracker formula (in parts).

Flour	68.5
Water	22.0
Shortening	8.0
Salt	1.0
Soda	0.3
Yeast	0.2
TOTAL	100.0

Although the shortening value of a fat which is to be used in crackers is an important consideration, the chief emphasis in the selection of a fat for this purpose is placed upon stability. Soda crackers, unlike bread and many other products, cannot be baked in small establishments and distributed locally, with a quick turnover in sales and consumption. On the contrary, the complicated and expensive machinery required for making crackers has largely confined the manufacture of this commodity to a relatively few large establishments. Crackers are now sold almost exclusively in small, individual packages, which may be stored for months in warehouses or on dealers' shelves before the contents are consumed.

The broad subject of the stability of fats in baked products has been discussed in a preceding paragraph (page 287). As mentioned previously, soda crackers are more liable to become rancid than other packaged products because they contain no sugar to serve as an antioxidant for the fat which they contain.

The most stable fats available for cracker manufacture are all-hydrogenated shortenings of the special biscuit and cracker type. Such shortenings have a stability, as measured by the Swift accelerated method, of 120 hours or more, as compared with 8 to 12 hours for most lards and oleo oils. It should not be inferred, however, that crackers made with biscuit and

[20] A. S. Richardson, H. S. Coith, and V. M. Votaw (to Procter and Gamble Co.), U. S. Pat. 2,132,700 (1938).

sale shift in baking practice has resulted partly from changes in the living habits of the American people, but is also attributable in some degree to improvements in baking technology. Home baked bread is no longer comparable in quality to the uniformly good product of modern, scientifically operated bakeries. Within recent years there has been a notable improvement in the average quality of bakers' cakes, and there is reason to believe that the factors which have operated to take bread baking largely out of the home may eventually lead to a similar decrease in the proportion of home baked cakes.

Cake is distinctive among baked products for its combination of extreme sweetness with a highly developed cellular structure. To dissolve the large proportion of sugar used in its composition, cake dough must contain a high percentage of liquids. Hence cake doughs are thinner and more fluid than those of other classes of baked goods. In order for the relatively watery cake dough to rise and assume the desired form in the baking operation, its structural requirements are extremely critical. As explained previously, the shortening used in a cake plays a predominant role in determining this structure. Consequently, the quality requirements for cake making fats are much more exacting than for fats which are to be used for most other baking purposes.

The cakes which contain fats may be divided into two main classes, namely yellow cakes, in which whole eggs or egg yolks are used, and white cakes, which are made only with egg whites. The two classes differ considerably both in the characteristics of the finished products and the behavior of their doughs. The so called "sponge cakes" constitute a third class, but as these are made without the use of shortening, they are outside the scope of the present discussion.

The essential ingredients in a yellow cake are flour, sugar, shortening, and whole eggs or egg yolks. Small quantities of salt and flavoring extracts are used for flavor, and unless a very high percentage of eggs is used, milk is also added to provide the necessary amount of liquids in the dough. Baking powder or a similar leavener is used in all cakes except the higher fat content pound cakes. Based on 100 parts of flour, the approximate range within which the other major ingredients may be varied is as follows:

Flour	(100 parts)
Sugar	80–140
Shortening	20–100
Eggs	20–100
Milk	0–100

There are a number of reasons why the above proportions must be adhered to. In order that the cake may be characteristically "rich" in taste, and not "bready," the shortening content must be fairly high. Usually it is not less than about 35% of the weight of the flour, or more than about

50% In cakes of the pound cake type however the fat content may amount to as much as 100% of the weight of the flour

Practically all cake formulas require an amount of eggs equal to or greater than the amount of shortening The use of an excess of shortening with too little eggs produces a poor dispersion of fat in the dough with consequent impairment of volume and texture in the finished cake Cakes with an excessively high ratio of fat to eggs are also inclined to give the impression of greasiness An excess of eggs much beyond that required by the shortening is seldom used because eggs are normally the most expensive ingredient in the dough Pound cakes which are very rich in fat are correspondingly high in egg content

The proportions of milk and eggs in a cake formula are related since both are liquid ingredients When the fat in the mixture consists of ordinary shortening the weight of milk is usually about equal to the weight of eggs In a very rich pound cake formula the milk may be reduced much below the weight of the eggs and in formulas for superglycerinated fats the milk may exceed the eggs in amount by as much as 100% With ordinary shortenings the usual proportion of liquids (eggs and milk combined) is about 100% of the weight of the flour With superglycerinated shortenings the liquids may be increased to as much as 165% of the weight of the flour A cake containing too little liquids will not only be dry and unpalatable but also will have a harsh texture If too great a quantity of liquids is used in the cake the structure will be unduly weakened and it will be likely to fall or collapse in the oven

The amount of sugar that can be used is determined by the liquid content of the cake In no case can the sugar exceed about 85% to 95% of the combined eggs and milk as starch in the flour will fail to gel in the presence of stronger sucrose solutions [27] The strong emulsifying properties of the superglycerinated shortenings contribute to the strength of the dough sufficiently to permit the incorporation of sufficient liquids to make the sugar content equivalent to as much as 140% of the weight of the flour Cakes made with a high ratio of sugar to flour are commonly termed high ratio cakes The maximum amount of sugar which can be incorporated in a cake depends to some extent upon the form in which the cake is to be baked Thin layers and sheets require less structural strength and may contain more liquids and sugar than loaves or other relatively thick forms

Typical formulas for different varieties of yellow cakes are shown in Table 114 Various optional ingredients such as nuts fruits spices chocolate etc may of course be incorporated in the basic yellow cake dough

Three basic methods are employed in combining the ingredients of cake doughs These are the sugar batter the flour batter and the single

[27] In this connection see S Woodruff and L Nicoli *Cereal Chem* 8 243–251 (1931)

stage" methods In the sugar batter procedure, sugar and fat are first creamed together, creaming is continued with addition of the eggs, and the mixing operation is finished by adding the milk and the flour, in alternate small portions This method of mixing has the advantage of producing a maximum incorporation of air in the fat, and of avoiding excessive working of the flour

In the flour batter procedure, the fat is creamed with the flour, and the eggs and sugar are beaten together in a separate bowl The two mixtures are then combined, after which the milk is added This procedure does not produce a dough containing as much air as does the sugar batter method It also is somewhat inclined to overdevelop the gluten in the flour, with consequent toughening of the dough, although this tendency is perhaps unimportant where cake flour of good quality is used The chief advantage

TABLE 114
TYPICAL FORMULAS IN PARTS BY WEIGHT FOR DIFFERENT VARIETIES OF YELLOW CAKES

Ingredient	Ordinary yellow cake	High ratio (loaves)	High ratio[a] (layers)	Pound cake
Sugar	25 5	29 6	29 8	24 6
Fat	13 4	11 4	11 6	20 0
Whole eggs	14 8	11 4	12 6	24 6
Milk	14 8	22 5	22 2	5 0
Flour	29 8	22 5	21 2	24 6
Baking powder	0 7	1 3	1 3	—
Salt	0 6	0 8	0 8	0 7
Flavor	0 4	0 5	0 5	0 5
TOTAL	100 0	100 0	100 0	100 0

[a] Suitable for use with superglycerinated shortenings

of the flour batter method is that it is very effective in dispersing and distributing the fat through the dough It thus produces a cake of fine grain and texture, and permits the use of higher proportions of sugar and liquids than the sugar batter procedure

The single stage method[21] involves nothing more than simply placing all the major ingredients in the bowl at once and mixing The baking powder is added near the end of the mixing period Its advantages in convenience and simplicity are obvious, but it does not produce cakes of quite as good volume as those mixed by the other methods, and hence is not widely used

For mixing high ratio cakes, a modification of the flour batter process is recommended However, this modification, unlike the ordinary flour batter method, does not require the use of two mixing bowls The procedure is to first cream the fat with the flour, then add the sugar and part of the milk, and then mix in the eggs and the remaining milk None of the mixing stages are prolonged, and the entire operation is carried out with

the mixing machine running at low speed In ordinary cake mixing the creaming stages are conducted at second or medium speed

Cakes made to a high ratio formula with the use of large proportions of sugar and milk possess a number of points of superiority over ordinary cakes They are sweeter more tender and more moist and they dry out less rapidly Also since sugar and milk are relatively cheap they are less expensive to make Their disadvantages are that they are relatively fragile and that they are too light and fluffy and too sweet for some tastes Regardless of the merits of the high ratio formulas however there can be little argument as to those of the superglycerinated shortenings as these materials will produce a cake of superior grain and texture when used in any formula The high degree of fat dispersion obtainable with a superglycerinated shortening in a non high ratio dough as compared with that obtainable with an ordinary shortening is evident from a comparison of Figures 28 (page 276) and 37

From a purely physical standpoint butter is not a superior cake making material It does not cream particularly well and is notably lacking in uniformity On the score of flavor however butter has no satisfactory substitute The use of butter in a cake imparts a desirable flavor to the product which is impossible to obtain with any other shortening material It is noteworthy that margarines which simulate butter very closely when used as table spreads fail to impart any considerable amount of butter flavor to cake or other baked products For cake baking relatively strong flavored butters are preferred such as would not ordinarily be considered most desirable for table use

Tastes differ so greatly that it is difficult to say what constitutes the best possible shortening material for cake baking However it is the opinion of at least a good many bakers that the best possible product is obtained with a mixture of superglycerinated shortening and butter, in a formula which contains more sugar than the older commercial recipes but somewhat less than the true high ratio formulas

Salad and cooking oils are inapplicable to cake making Oleo oil is seldom used principally because of its short plastic range Margarine, for the reasons stated above possesses little or no advantage over ordinary shortenings Shortenings of the all hydrogenated and to a lesser extent the compound types have been much used in the past by commercial cake bakers but have now been supplanted to a large extent by superglycerinated shortenings The use of these shortenings and certain related materials in cake making is covered by patents[23-25]

[23] H S Coith A S Richardson and V M Votaw (to Procter and Gamble Co) U S Pats 2 132 396-97 (1938)

[24] B R Harris U S Pats 2 024 357 (1935) (to Procter and Gamble Co) 2 132 416 (1938) 2 132 417 (1938) 2 132 687 (1938)

[25] B R Harris (to Procter and Gamble Co) U S Pat 2 158 775 (1939)

As a fat for cake making, lard is used very little in the household, and hardly at all in commercial bakeries. One reason for the limited use of lard in cake making is the characteristic odor and flavor of this fat, which is not considered desirable in cakes. Another reason is its poor creaming quality. Cake doughs made with lard (Fig. 38) are virtually devoid of incorporated air.

A considerable amount of work has been done in an effort to develop special methods and formulas which will permit the manufacture of good

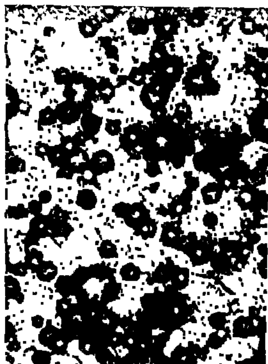


Fig. 37.—Photomicrograph (× 290) of pound cake dough made with super glycerinated shortening.

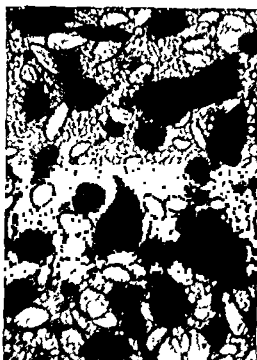


Fig. 38.—Photomicrograph (× 290) of yellow cake dough made with lard.

cakes from lard. The investigations of Swartz[26] and Baeder[27] are typical of those concerned with yellow cakes. The special methods produce cakes which are considerably better than lard cakes mixed by conventional methods. Some of the cakes made with lard are of sufficiently good quality to compare very favorably with cakes made with shortenings, in acceptance tests among lay judges. However, none of the special formulas and methods will produce yellow cakes from lard which are of the highest quality.

[26] V. Swartz, *Baker's Helper*, 67, 844–846, 1082–1084 (1937).

[27] H. Baeder, "The Use of Lard in Cake Making," *Nebraska Agr. Expt. Sta. Bull.* No. 320 (1938).

according to the standards of professional bakers. Due to the lack of air in the dough, the cakes are of poor grain and texture and, although the flavor of the lard may be well disguised, its odor is still apparent to close observation, especially in freshly cut slices of the cake.

The new deodorized lard products which have been placed on the market in limited quantities within the past few years are much superior to ordinary lard for cake making, as they cream well and are neutral in flavor and odor. As mentioned previously, however, the utility of these products is limited by their variable tendency to lose air when mixed by the sugar batter method. Superglycerinated shortenings are not made at present from either lard or hydrogenated lard, although from a technological standpoint such products are of course perfectly feasible. The addition of mono- and diglycerides to hydrogenated lard to convert it to a superglycerinated shortening material does not eliminate its tendency to lose air in the later stages of the mixing process and in fact may accentuate this tendency.

TABLE 115

TYPICAL FORMULAS IN PARTS BY WEIGHT FOR ORDINARY AND HIGH RATIO WHITE CAKES

Ingredient	Ordinary white cake	High ratio white layers
Sugar	25.8	29.3
Fat	13.0	11.5
Egg whites	17.8	15.7
Milk	15.4	20.0
Flour	25.8	20.9
Baking powder	0.9	1.3
Salt	0.6	0.8
Flavor	0.5	0.5
TOTAL	100.0	100.0

The ingredients used in the manufacture of white cakes are similar to those used in yellow cakes except that egg whites are substituted for whole eggs or egg yolks.

The proportions of the ingredients in white cakes are but little different from those in yellow cakes, although ordinarily 25% to 35% more egg whites are used than whole eggs. Non-high ratio white cakes are usually made a little sweeter than corresponding yellow cakes. Typical formulas for ordinary and high ratio white cakes are given in Table 115.

White cakes are in general inclined to rise somewhat less than yellow cakes and to have a finer grain and be less inclined to develop large cavities and tunnels. Most white cake is baked in the form of sheets and layers. White loaves are much less common than yellow loaves.

White cake doughs behave differently in some respects from yellow cake doughs. The differences are undoubtedly due to the absence in white

As a fat for cake making, lard is used very little in the household, and hardly at all in commercial bakeries One reason for the limited use of lard in cake making is the characteristic odor and flavor of this fat, which is not considered desirable in cakes Another reason is its poor creaming quality Cake doughs made with lard (Fig 38) are virtually devoid of incorporated air

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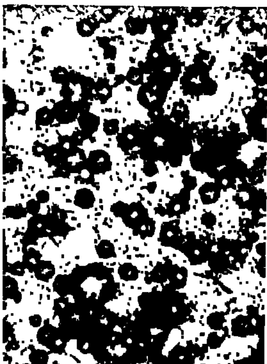


Fig 37 —Photomicrograph (× 290) of pound cake dough made with super glycerinated shortening



Fig 38 —Photomicrograph (× 290) of yellow cake dough made with lard

cakes from lard The investigations of Swartz[26] and Baeder[27] are typical of those concerned with yellow cakes The special methods produce cakes which are considerably better than lard cakes mixed by conventional methods Some of the cakes made with lard are of sufficiently good quality to compare very favorably with cakes made with shortenings, in acceptance tests among lay judges However, none of the special formulas and methods will produce yellow cakes from lard which are of the highest quality

[26] V Swartz, *Baker's Helper*, 67, 844–846, 1082–1084 (1937)

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TABLE 115

TYPICAL FORMULAS IN PARTS BY WEIGHT FOR ORDINARY AND HIGH RATIO WHITE CAKES

Ingredient	Ordinary white cake	High ratio white layers
Sugar	25 8	29 3
Fat	13 0	11 5
Egg whites	17 8	15 7
Milk	15 4	20 0
Flour	25 8	20 0
Baking powder	0 9	1 3
Salt	0 6	0 8
Flavor	0 5	0 5
TOTAL	100 0	100 0

ening material does not eliminate its tendency to lose air in the later stages of the mixing process and in fact may accentuate this tendency

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White cake doughs behave differently in some respects from yellow cake doughs The differences are undoubtedly due to the absence in white

doughs of lecithin, lecithoprotein compounds, or other surface active substances, which are present in egg yolks

In white cake doughs, as in yellow doughs, the incorporated air is invariably enclosed in the fat phase However, the fat particles assume a form somewhat different from that observed in yellow doughs the fat does not appear to spread in layers to any extent, but rather is in the form of small masses which tend to approach a globular form, and which exhibit a sharp line of demarcation between the aqueous and fat phases (see Figs 28, page 276, and 39)

In the manufacture of yellow cakes, the leavening action obtained is related to the amount of air which is incorporated in the fat Provided that the cake suffers no collapse of its structure while in the oven, the loaf volume obtained with a given formula is *directly proportional to the in-*



FIG 39 —Photomicrograph (× 290) of white cake dough

corporation of air In the case of white cakes, however, no such direct relation exists The different manner in which white and yellow cake doughs respond to increases in their air content is illustrated by the tests detailed in Table 116 In these tests, identical formulas and methods of mixing were used in the preparation of the comparative cakes, but shortenings of different creaming capacities were used, in order to obtain doughs of different air content

Because of the fact that white cakes are not highly dependent upon a large incorporation of air for their good qualities, comparatively good white cakes may be made from the poorer creaming fats The method and formula of Swartz,[28] for example, produce a cake from lard which is entirely acceptable in all respects, except perhaps for a slight lardlike odor De-

[28] V Swartz, *Baker's Helper*, 69, 734, 752, 70, 41–42 (1938).

odorized lards or hydrogenated lards yield cakes of excellent quality. The best results in the manufacture of white cakes as well as yellow cakes, however, are probably obtained with the use of superglycerinated shortenings, with the addition of a certain proportion of butter, if a butter flavor is desired.

The customary methods of mixing white cakes are in most respects not different from those employed in making yellow cakes. However, it is a quite common practice to beat the egg whites apart from the other ingredients before adding them to the mix. There is no evidence that this results in any significant improvement of the dough or cake. Separate beating of the eggs certainly adds nothing to the amount of air incorporated in the dough, either in the case of white or yellow cakes. Microscopic observation reveals that air is entrapped only in the fat phase of the finished dough, regardless of the method followed in combining the ingredients, and the

TABLE 116

EFFECT OF INCREASING AIR INCORPORATED IN WHITE CAKE DOUGH, IN COMPARISON WITH YELLOW DOUGH

Kind of cake	Air in dough % by vol. on basis of the fat	Loaf volume cc./lb.
White	245	1225
White	350	1215
Yellow	190	1245
Yellow	250	1360
Yellow	270	1380

maximum air carrying capacity of the fat is easily approached by ordinary methods of mixing.

(e) Biscuits, Wafers, and Cookies

The various commercially baked cookies, wafers, sweet biscuits, etc. are all quite similar in structure and appearance. They consist of thin crisp products of low moisture content, which are baked from a stiff sweet dough. The dough is either rolled into a thin sheet, from which the individual biscuits are cut, or else is extruded through a die and sliced into thin sections by a wire cutter. Most retail bakeries do a considerable volume of business in cookies and similar products. In addition to the fat used by the smaller bakeries in this class of goods, great quantities of fats are consumed by large manufacturers of packaged sweet goods, whose output includes a wide variety of items, with and without fruit, cream and other fillings and coatings.

The essential difference between these products and ordinary cake is their low content of moisture. Whereas the sugar in ordinary cakes is in the

form of a liquid and mobile syrup, that in cookies may be solidified to a candylike mass Sufficient fat must be present to break the continuity of this mass, otherwise the product will be impossibly hard and refractory Most cookies, etc, contain about the same proportions of fat as yellow and white cakes, namely 10% to 15%

It is desirable for the fat to contribute some degree of leavening to this class of products However, the leavening is much less critical than in the case of cakes and in choosing a shortening for biscuits and cookies the chief emphasis is placed upon shortening value and stability, rather than creaming and emulsifying properties

The fats which are used for these products are principally lard, oleo oil and all hydrogenated vegetable shortenings Lard has the advantage of being high in shortening value, whereas oleo oil and all hydrogenated shortenings have the advantage of being more stable than lard

(f) Pie Crust

Pie crust consists essentially of flour and fat, mixed with a little salt and water However, in some commercial formulas small proportions of sugar and eggs are used The amount of fat in the formula may vary from as little as 30% to as much as 60% but is usually in the neighborhood of about 40% A liberal proportion of fat in the dough not only makes the crust tender, but also prevents it from readily becoming soggy, from absorption of the watery ingredients of the pie filling

Most pie crust is of the so called "flaky" variety In making this variety of pastry, a fine dispersion of the fat throughout the dough is not desired—on the contrary, it is essential that the dough be but slightly mixed, in order that the fat may be incorporated in the form of relatively large masses When the dough is rolled out into a sheet the fat is pressed into the form of flat layers, dispersed along parallel planes through the crust After the crust is baked, these layers of fat provide planes of cleavage parallel to the surface of the crust The crust is consequently inclined to disintegrate in the form of flakes rather than crumbs Obviously a plastic fat is required for making a flaky pie crust A "crumbly" crust is also sometimes prepared, by using a very high proportion of fat or even a liquid oil, and mixing the fat and flour very thoroughly This produces a fragile crust in which the surfaces of cleavage are neither plane nor parallel, but extend in all directions

The requisites of a good pie crust shortening are plasticity and a high shortening value Ability to cream, ability to emulsify, and stability are unimportant Lard is much used for pie crust It is superior to most other fats in shortening power, and in pies its characteristic odor and flavor are considered desirable by many bakers The hydrogenated and deodorized lards also have good shortening qualities in pie crust, and have

the advantage over ordinary lard of having neither flavor nor odor, in cases where a completely neutral product is desired Compound type and all hydrogenated shortenings are also used in considerable quantities in pie crust

(g) *Danish and Puff Pastry*

The manufacture of puff pastry and pastry of the Danish type requires a shortening material of a somewhat special variety In these products, the distribution of fat in the dough is somewhat similar to that in ordinary flaky pie crust However, this distribution is attained, not by mixing the fat in the dough, but by rolling it in after the dough is mixed

The original dough may vary considerably in composition, and may or may not be yeast-leavened It is essential, however, that it have the property of ready extensibility, *i e*, it must be soft enough to roll out readily, but tough and coherent enough so that the rolled sheets will not easily tear or come apart in rolling and handling Generally no large amount of fat is used in making up the original dough, but it is usual to roll in a quantity of fat greater in amount than the dough in which it is incorporated, so that the finished product is very high in fat content

The "rolling in" operation is initiated by forming the dough into a thin, roughly rectangular sheet Then, beginning at one end of the sheet, a layer of fat is spread over two thirds of its surface The ungreased third of the sheet is then folded over on the middle portion of the sheet, and the remaining one third, which has been covered with fat, is folded on top of the ungreased surface This operation produces a new sheet, consisting of three layers of dough, separated by two layers of fat The new sheet is then rolled out to the size of the original sheet, the latter is again spread with fat and folded, and the rolling, fat spreading, and folding is continued for a number of times

As each complete cycle of operations increases the number of layers threefold, the ultimate result is a laminated sheet, consisting of a great many very thin alternate layers of fat and dough When the product is baked, the layers of dough tend to separate, from the expansion of air or water vapor entrapped between them This produces a leavening action, and causes the product to rise in the oven

In making this variety of pastry the best results are obtained with special pastry margarines or "puff pastes," which have been compounded to yield a tough, waxy fat, of good extensibility For the manufacture of pastry shells of the puff pastry type, the use of special "puff paste" is more or less essential For certain sweet pastries, however, in which a yeast leavened dough is used, and in which it is not necessary for the layered structure of the product to be so precisely developed, any one of a variety of fats may be used, including margarine, butter, and the vegetable shortenings

(h) Doughnuts and Other Fried Products

Doughnuts, crullers, and related products comprise a class of goods which are not baked in an oven, but are deep fried in hot fat In the United States, much the greater portion of these products consists of doughnuts, although in some sections of the country there is a considerable production of crullers and of fried pies

Little fat is used in the preparation of doughnut or cruller dough, but the dough will absorb a considerable quantity of fat in frying The usual fat content of doughnuts is not less than 20%

The subject of commercial food frying has been discussed at some length in previous paragraphs It may be added here that, in addition to the factors discussed previously, the rate at which fats tend to be absorbed by doughnuts is of some consequence to commercial fryers of this product If a fat is absorbed to an undue extent, it will not only produce an unduly greasy doughnut, but will also be expensive to use, since the fat is usually higher in price than most of the other ingredients

The question of fat absorption in the case of different varieties of fats is somewhat controversial The best opinion seems to be that there are no significant differences in this respect among the different edible fats and oils The unusually extensive tests of Lantz and Carlin[15] reveal considerable differences among five representative lots of vegetable shortenings, but it is uncertain to what extent these are due to unavoidable variables in the frying operation Their figures for absorption, in terms of ounces of fat absorbed per dozen doughnuts (about 12 ounces) are as follows

Shortening No 3 (all hydrogenated type)	1 646
Shortening No 2 (all hydrogenated type)	1 682
Shortening No 5 (compound type)	1 762
Shortening No 4 (all hydrogenated type)	1 777
Shortening No 1 (compound type)	1 792

It will be seen that the shortening exhibiting the highest absorption is absorped to the extent of approximately 8 9% more than that with the lowest absorption

Lantz and Carlin also state that the fats tested show wide variations in absorption during the first four days that they were used, after which their rates of absorption became more or less constant Thus it appears that the tendency of a fat to be absorbed in doughnut frying cannot be evaluated except upon the basis of extended tests

(i) Cream Icings

Considerable quantities of fat are consumed by commercial bakers in the manufacture of cream icings, for cakes and similar goods This product consists basically of fat, powdered sugar and milk, with a consid

erable quantity of air beaten into the fat The following formula (in parts) is typical of cream icing in its simplest form

Fat	25 0
Powdered sugar	50 0
Milk	23 8
Salt	0 6
Flavor	0 6
TOTAL	100 0

The fat most commonly used for cream icings is an all hydrogenated vegetable shortening to which butter is sometimes added for flavor Superglycerinated shortening produces an icing which is smoother and more stable than ordinary shortening Shortenings of the compound type are usually not sufficiently neutral in flavor for good cream icings Lard is unsuitable for icings both because of its flavor and its lack of creaming ability A deodorized lard product which has been stiffened by hydrogenation or the addition of highly hydrogenated lard may be used satisfactorily The fat used in cream icings must be sufficiently firm to remain plastic at the highest temperature to which the icing is to be subjected as the body of the product depends upon the plastic properties of the fat

Cream icing is essentially an emulsion of sugar syrup sugar crystals fat and air according to the formula the fat may be either the continuous or the discontinuous phase

(g) Biscuit Fillings and Coatings

Certain varieties of packaged sweet biscuits are prepared with coatings which have a fat base For this purpose a fat with a short plastic range is desirable The biscuits will retain their form and appearance better in the package if the fat is quite firm or even hard at ordinary temperatures However it must melt or at least soften readily in the mouth Thus the fats which are most suitable for this purpose are similar in properties to confectioner s fats rather than the plastic fats previously described

Various so called enrobing fats for biscuits are marketed under proprietary names Their formulas are generally considered secret however they appear for the most part to be composed of partially hydrogenated coconut oil or coconut oil stearines blended in some cases with other hydrogenated vegetable oils

5 Confectioners' Fats

Most of the fat consumed in candies consists of cocoa butter in the form of chocolate Chocolate which is the product obtained by grinding roasted cocoa beans contains approximately 50% of fat and 50% of solid material In the manufacture of chocolate candies the solids content of the chocolate is greatly increased by the addition of sugar, hence in order to maintain

a suitable consistency in molten chocolate coatings it is necessary to add fat beyond the amount normally present in the chocolate[29] The amount of fat added may vary from 15% to 25% in ordinary coatings, to 35% or more in milk chocolates In the case of candies which are labeled as chocolates, the added fat must be pure cocoa butter, cheaper products such as five cent candy bars, which are not designated as chocolates, may contain less expensive fats The coating fats used in the United States as substitutes for cocoa butter consist principally of stearines pressed from coconut, palm kernel or other lauric acid oils In Europe there is some use of Borneo tallow and other less common vegetable butters A very short plastic range is of course essential in a coating fat, as the coating must be non greasy at ordinary temperatures, but must melt in the mouth

The commercial machine coating of candies is quite critical insofar as the properties of the coating fats are concerned, inasmuch as the coatings must be capable of being quickly transformed from viscous, semiplastic suspensions to hard, nongreasy solids The crystallization habits of the fat, the rapidity with which it solidifies, its tendency to supercool, the temperatures at which it melts and solidifies, its tendency toward polymorphism, are all extremely important Fats other than cocoa butter, or fat mixtures, behave differently from pure cocoa butter, and require corresponding adjustments in the coating process Occasional lots of cocoa butter are encountered which exhibit a sufficiently abnormal behaviour to cause trouble in the coating procedure applicable to normal cocoa butters For the evaluation of cocoa butter and other coating fats the standard solidification test proposed by Jensen[30] is recommended

In the case of chocolate confections which are to be molded, the volume change of the fat upon solidification is important since a considerable shrinkage is necessary for good molding properties In addition to the coating fats consumed in candies, considerable quantities of fats of this type are also used in coating ice cream bars and sweet biscuits

Although the coating fats comprise the most important group of confectioners' fats, there is a considerable consumption of other fats in candies Cocoa butter, coconut oil, oleo oil, and butter comprise some of the materials used A few manufacturers of hydrogenated vegetable oils prepare special confectioners' fats One of these consists of oil hydrogenated selectively to obtain a short plastic range, but with a melting point substantially above that of ordinary hydrogenated shortenings This product is said to be particularly suitable for the manufacture of caramels

[29] The addition of lecithin to the coating reduces its viscosity and minimizes the amount of fat which must be added For a complete discussion of the surface activity of lecithin in chocolate suspensions see R Whymper, *The Problem of Chocolate Fat Bloom*, Manufacturing Confectioner Pub Co , Chicago

[30] H R Jensen, *The Chemistry, Flavouring, and Manufacture of Chocolate Confectionery and Cocoa* Blakiston, Philadelphia, 1931

CHAPTER XII

SOAP AND OTHER SURFACE-ACTIVE MATERIALS

1. Introduction

There are a variety of oil and fat derivatives which owe their industrial importance to their ability to modify the surface behavior of liquids in which they are dissolved These products may be grouped under the broad designation of "surface active materials "[1] According to their various uses, they are classified as detergents, wetting agents, emulsifying agents, dispersing agents, frothing agents, etc The most important surface active material is ordinary soap Other materials derived from fats and oils include certain detergents other than soap, sulfonated oils for textile and leather processing, and a great variety of emulsifying and wetting agents which find special applications in many different industries

Fats and oils, or rather fatty acids—for the latter are usually the essential materials—are peculiarly suitable for the production of surface active agents because of their specific molecular structure The commercially available fatty acids consist for the most part of straight hydrocarbon chains of 12 to 18 carbon atoms, terminating in a reactive carboxyl group When the terminal hydrogen atom is substituted with an alkaline metal or when the carboxyl group is otherwise converted to a group of hydrophilic nature, the resulting molecule becomes endowed with certain peculiar properties The hydrocarbon end then will have an affinity for fatty oils, aliphatic hydrocarbons, and similar long chain compounds, whereas the opposite end of the molecule, at some distance removed, will have an attraction for water or aqueous solutions Thus within the same molecule there will be a dual affinity for substances of entirely different nature Further-

[1] GENERAL REFERENCES N K Adam *The Physics and Chemistry of Surfaces*, 2nd ed , Oxford Univ Press, London, 1938 J Alexander, ed , *Colloid Chemistry*, Vol I, Chemical Catalog Co , New York, 1926 S Berkman and G Egloff, *Emulsions and Foams*, Reinhold, New York, 1941 D Burton and G F Robertshaw, *Sulphated Oils and Allied Products*, Chemical Pub Co , New York, 1940 W Clayton, *The Theory of Emulsions and Their Technical Treatment* 4th ed , Blakiston, Philadelphia, 1943 H Freundlich *Colloid and Capillary Chemistry* trans from 3rd German ed by H S Hatfield, Methuen London, 1926 G Hefter and H Schonfeld, *Chemie und Technologie der Fette und Fettprodukte*, Vol IV, Springer, Vienna 1939 T P Hilditch, *The Industrial Chemistry of the Fats and Waxes* 2nd ed , Baillière, Tindall & Cox, London, 1941 International Society of Leather Trades' Chemists, British Section, *Wetting and Detergency*, 2nd ed , Chemical Pub Co , New York, 1939 E G Thomssen and C R Kemp, *Modern Soap Making*, MacNair Dorland, New York, 1937

more, the two ends of the molecule will be sufficiently separated for the two affinities to come into simultaneous and independent action

The aforementioned dual nature of the molecule is an essential condition if the substance is to have surface activity, as will be more readily apparent from the ensuing discussion of the theory of surface action In most cases, the size or length of the molecule is also somewhat critical, it has been claimed that the properties of a surface active agent depend to some degree upon the balance existing between the hydrophilic and lipophilic portions of the molecule,[2 3] as determined by the chain length The optimum chain length in surface active compounds is somewhat variable, according to the intended uses of these materials However, in general it will be found to be within the same range as the chain length of the common fatty acids, viz 12 to 18 carbon atoms

Surface active molecules with long hydrocarbon chains can be built with ease only from fats or fatty acids Aside from these raw materials, petroleum is the only reasonably cheap source of such chains However, the utilization of petroleum in the manufacture of surface active substances presents difficulties, both in introducing polar or hydrophilic groups at the end of the chain and also in maintaining the chain at the proper length

2 Theory of Surface Action

The modern theory of the mechanism of surface action is intimately related to the fundamental work of Harkins[4] and Langmuir[5] dealing with the phenomenon of molecular orientation at interfaces

As mentioned previously, all substances capable of surface action are composed of relatively large molecules, which contain widely separated groups of dissimilar nature It is also characteristic of these materials that they exert their useful effect in quite dilute solution Their ability to function effectively in low concentrations is due to the tendency of the molecules to concentrate at interfaces between the solvent and solids, gases, or other immiscible liquids At the boundaries of the solvent there is an orientation of the molecules according to the nature of the substances forming the interface If the solvent is of an oily nature, the lipophilic hydrocarbon chain or "tail" of the molecule will be oriented toward the solvent, and the hydrophilic or polar "head" will be directed toward the other phase If, as is more usually the case, the solvent is aqueous, the

[2] B R Harris, A K Epstein, and F J Cahn, *Oil & Soap*, **18**, 179–182 (1941)

[3] F D Snell, *Ind Eng Chem*, **35**, 107–117 (1943)

[4] J Alexander, editor, *Colloid Chemistry* Vol I, Chemical Catalog Co , New York, 1926, pp 192–264 Also W D Harkins, F E Brown and E C H Davies, *J Am Chem Soc* **39**, 354 364 (1917), W D Harkins, E C H Davies, and G L Clark *ibid*, **39**, 541–596 (1917)

[5] See J Alexander, *op cit*, pp 525–546 Also I Langmuir, *J Am Chem Soc*, **39**, 1848–1906 (1917)

head of the surface-active molecules will be imbedded in the solvent phase and the tail will be directed outward In a great many practical applications, the surfaces in question are those of two immiscible liquids, one of which is aqueous and the other oily In such cases, the surface active agent distributes itself at the interface, with the heads of the molecules in the water and "tails" in the oil

When an interface is freshly established in the presence of a surface active agent, the molecules of the latter must not only become properly oriented before they can function, but must also migrate to the interface from adjacent portions of the liquid A sufficient degree of orientation and migration to establish equilibrium conditions may require an appreciable time In practical applications, therefore, the speed with which an agent acts must sometimes be considered, as well as its ultimate effectiveness The effectiveness of a surface active agent under static conditions (with equilibrium established) may be somewhat greater than under dynamic conditions (which produce a series of constantly renewed interfaces)

The practical effect of the interfacial absorption and orientation of surface active agents may be manifested in a number of different ways At liquid–gas interfaces the strength of the liquid film is lowered, so that it is more easily broken by mechanical influences In such a case, the surface-active agent promotes foaming and suds or lather formation At liquid solid interfaces a similar weakening of the liquid film occurs, rendering the liquid less coherent within itself and more adherent to the solid surface This promotes wetting of the solid, which in turn causes the liquid to spread upon the solid surface and to penetrate minute pores or openings It is to be noted that the promotion of wetting can be reversed by the application of suitable materials to the solid Thus in the treatment of fabrics for water repellency the fibers of the fabric are coated with materials which are hydrophobic in nature and inhibit wetting to such an extent that water is unable to penetrate the fabric pores

From the industrial standpoint a highly important case of surface action is that occurring between two immiscible liquids, as oil and water In this case the presence of surface active molecules at the interface makes the latter more readily extensible, so that upon agitation one phase may be more easily broken up into small droplets and dispersed in the other to form an emulsion After the emulsion is formed, molecular orientation of the surface active molecules at the surface of the droplet forms a protective film which prevents the droplets from coalescing upon contact with each other

(a) *Quantitative Evaluation of Factors Influencing Surface Action*

The operations in which surface action is important, including foaming and defoaming, wetting and dewetting, emulsification and de emulsifica-

tion, and flocculation and deflocculation, all involve the extension or restriction of liquid–liquid, liquid–solid, liquid–gas, or solid–gas interfaces Changes in surface or interfacial area are associated with corresponding and definite changes in the free surface energies of the surfaces involved, consequently, these operations are susceptible to mathematical treatment

Numerically, the free energy of a surface, in terms of ergs per sq cm, is equal to the surface tension, expressed as dynes per cm Theoretically, therefore, any surface active material may be evaluated in terms of its effect on the surface tensions of the various surfaces in the system in which it is involved

Surface tensions of gas–liquid and liquid–liquid systems may be easily and accurately measured by a variety of methods There are at present no methods, however, for determining surface tensions at solid–gas and solid–liquid interfaces

The characteristic angle at which a liquid meets a solid surface with which it is in contact, termed the *contact angle*, is important in considerations of wetting and detergency, and may be measured by suitable means, even when the solid is in the form of a powder[6] Contact angles may vary from 0°, indicating complete wetting of the solid, to nearly 180°, in the case of almost complete lack of wetting, or in other words, lack of adhesion between solid and liquid

Contact angles are directly related to the surface tensions existing at the various interfaces in the system The relationships between contact angles and surface tensions have been well stated by Adam,[1] from whom the following equations are taken

For the contact angle, θ, of a liquid in contact with a solid in air

$$\cos \theta = \gamma_{SA} - \gamma_{SL}/\gamma_{LA} \qquad (1)$$

where γ_{SA} = interfacial tension, solid–air, γ_{SL} = interfacial tension, solid–liquid, and γ_{LA} = interfacial tension, liquid–air

For the contact angle, θ_A, of a liquid, A, in contact with a solid and another liquid, B

$$\cos \theta_A = \gamma_{BS} - \gamma_{AS}/\gamma_{AB} \qquad (2)$$

where γ_{BS} = interfacial tension, liquid B–solid, γ_{AS} = interfacial tension, liquid A–solid, and γ_{AB} = interfacial tension, liquid A–liquid B The contact angle, θ_B, of liquid B, is, of course, the supplement of θ_A

Since surface tensions at liquid–solid and gas–solid interfaces are not measurable, certain other expressions avoiding these expressions are more

[6] S H Bell, J O Cutter, and C W Price, in International Society of Leather Trades' Chemists, British Section, *Wetting and Detergency* 2nd ed, Chemical Pub Co, New York, 1939, pp 19–24

useful than equations (*1*) and (*2*) The work of adhesion, W_{SL}, between a liquid and a solid in air is defined as follows

$$W_{SL} = \gamma_{SA} + \gamma_{LA} - \gamma_{SL} \qquad (3)$$

In the case of two liquids, A and B, in contact with a solid, the works of of adhesion W_{SA} and W_{SB} between the solid, and liquids A and B, respectively, are as follows.

$$W_{SA} = \gamma_A + \gamma_S - \gamma_{AS} \qquad (4)$$

$$W_{SB} = \gamma_B + \gamma_S - \gamma_{BS} \qquad (5)$$

Combining (*1*) and (*3*),

$$\cos\theta = \frac{W_{SL} - \gamma_{LA}}{\gamma_{LA}} \qquad (6)$$

Combining (*2*), (*4*) and (*5*),

$$\cos\theta_{AB} = \frac{(W_{AS} - \gamma_A) - (W_{BS} - \gamma_B)}{\gamma_{AB}} \qquad (7)$$

The quantities, $W_{AS} - \gamma_A$, $W_{BS} - \gamma_B$, and $W_{SL} - \gamma_{LA}$ are referred to as "adhesion tensions" They are a measure of the adhesion of the liquid for the solid minus the cohesion of the liquid, or in other words, of the tendency of the liquid to wet the solid

(*b*) *Foaming*

The formation of froth or foam on a liquid is accompanied by a tremendous extension of the liquid-air interface Consequently, foaming will be favored by the presence of any substance in the liquid which lowers the surface tension of the latter and decreases the work which must be done to extend the interface

Closely related to the readiness with which a liquid foams is the matter of stability of the foam Since the surface tension of the liquid tends constantly to diminish the surface, a low surface tension likewise contributes toward foam stability

It has been well established, however, that the surface tension of a liquid is not the decisive factor in determining whether it shall foam readily and produce a foam which is stable The effectiveness of certain surface-active materials in promoting and stabilizing foams appears to be due to their tendency to concentrate in the interface, and to their peculiar properties in concentrated surface films, rather than to their effect on the surface tension *per se*

That a solute must concentrate at the surface of a solution in order to lower the surface tension of the solvent liquid was demonstrated upon

theoretical grounds by Gibbs Discussions of the essential connection between surface concentration of solute and foaming capacity, upon the basis of the Gibbs equation have been presented in recent treatises by Clayton[1] and Berkman and Egloff [1]

Foulk,[7] in an investigation of foaming in solutions of organic compounds, found that stable foams were formed only when there was an appreciable difference between the static and dynamic surface tensions of the solution, or in other words, when there was a tendency of the dissolved substance to concentrate at the liquid–air interface Pure liquids are incapable of foaming Liquid films (of foams) are formed, according to Foulk's concept, by the near approach to each other of two liquid surfaces already formed A concentration gradient of dissolved substance in the film is considered essential to prevent the two surfaces from approaching to the point of coalescence

Adam,[1] in discussing the stability of foams, has emphasized the necessity of a stable film being able to easily and quickly vary in surface tension, both in order to meet permanent differences of stress in its different parts, and to absorb local mechanical shocks In this connection it is significant that most solutions of foam inducing substances (particularly those of low or medium molecular weight) exhibit their maximum foam producing capacities, not at concentrations at which surface tension is at a minimum, but rather at lower concentrations, where variation in concentration has a large effect on surface tension

There is evidence that some surface films, particularly those of the higher fatty acid soaps, actually exhibit plastic properties, due to the close packing of large molecules (Freundlich[1] and Wilson and Ries[8]) That such films would produce highly stable foams is obvious Adam considers that the speed with which surface active molecules can diffuse from the surface to the interior, and *vice versa* is probably important in determining the stability of the film He attributes the extreme persistence of concentrated soap foams to the probable slow diffusion of the large soap molecules It is noteworthy that in some instances, as for example in a solution of commercial lecithin in a fat or oil, the dissolved substance may contribute strongly to foaming without marked effect on the surface tension of the liquid

(c) *Emulsification*

An emulsion is usually defined as a system of two immiscible liquids, one of which is dispersed in the other in the form of small droplets This

[7] C W Foulk, *Ind Eng Chem* **21**, 815–817 (1929) C W Foulk and J N Miller, *ibid*, **23**, 1283–1288 (1931)

[8] R E Wilson and E D Ries, *First Colloid Symposium Monograph* Univ of Wisconsin, Madison, 1923, pp 145–170

definition must be broadened somewhat in order to include all of the systems which are commonly referred to as emulsions in industrial practice Virtually all industrially important emulsions consist of water or an aqueous solution and a fatty or hydrocarbon oil In oil and fat technology, particular attention must be given to emulsions in which one phase is a fat (which is a plastic solid), rather than a liquid oil Thus, for example, butter and margarine consist of a dispersed phase of watery droplets enclosed in a continuous phase of plastic fat A cake dough, on the other hand consists of a watery continuous phase surrounding a dispersed phase of plastic fat particles In a true water–oil emulsion the small dispersed particles are constricted to a spherical form by the forces of surface tension The fat particles in the dough, however, are not readily deformed, being plastic rather than liquid Consequently, they are of irregular rather than globular shape

All the surface active materials which are effective as emulsifying agents markedly lower the interfacial tension between the two liquid phases Since the interface must be very greatly extended in producing an emulsion, the energy considerations mentioned previously in connection with foams apply equally to the formation and the stability of emulsions In other words, lowering of the interfacial tension is in itself favorable to both the production of emulsions and their stabilization

While a low interfacial tension is undoubtedly an important factor in the production of a stable emulsion, it is by no means the only factor involved It is well recognized that the utility of an emulsifying agent in specific industrial applications cannot always be predicted simply from measurements of the degree to which this agent lowers the interfacial tension of the liquids in question Its effectiveness will be determined also by such considerations as the size and motility of the surface active molecules, and the degree to which they exhibit plasticity or rigidity in close packed layers in the interfacial film

The phenomenon of emulsification is rendered somewhat more complicated than that of foam formation by the existence of two liquid phases An emulsion of liquids *A* and *B* may consist of a dispersion of *A* in *B* or of *B* in *A* At first thought it might appear that the volume relationship between the two liquids would determine the type of emulsion *i e*, the liquid present in the lesser quantity would tend to become the disperse phase This, however, is not necessarily the case In some instances there is a tendency for the emulsion to break or to invert from one type to another if an attempt is made to increase the relative volume of the disperse phase beyond a certain point However, in many important emulsions, *e g*, in mayonnaise, the volume of the disperse phase greatly exceeds that of the continuous phase It is readily possible to prepare stable emulsions in which the volume of the inner phase exceeds that obtaining in

spherical close packing, and in which the globules of this phase are consequently deformed, if an emulsifying agent is used which markedly resists coalescence of the globules Actually, the question of which liquid shall be dispersed is determined by surface tension considerations which are definitely related to the nature of the emulsifying agent

The presently accepted theory relating to emulsion type was deduced by Bancroft and co workers[9] and has been confirmed by the work of Clowes[10] and others According to this theory, the film of oriented surface active molecules between the two phases of the emulsion is conceived to be in effect a third phase, possessing separate surface tensions against each of the two liquids which form the emulsion In the case of a water–oil emulsion, if the film has a greater affinity for water than for oil, its surface tension will be lower on the water than on the oil side The film surface will then tend to curve in such a direction as to reduce the total surface tension, *i e*, it will form a curve with the area of low surface tension on the outside and that of high surface tension on the inside, or will tend to enclose globules of oil in water If the film has a greater affinity for oil than for water, the effect will be reversed, and the tendency will be to form an emulsion of water in oil

In general, surface active agents which are freely soluble in water but sparingly soluble in oil will form emulsions of the oil in water type, whereas those more soluble in oil than in water will form emulsions of the water in oil type Thus sodium and potassium soaps stabilize oil in water emulsions, soaps of calcium or magnesium stabilize emulsions of the opposite type

The influence of the emulsifying agent upon the emulsion type is not absolute In some cases it is possible to produce an emulsion of one type by one method of mixing and of a reverse type by a different mixing procedure In other cases, as for example in the preparation of a cake dough the emulsion may invert from one type to another during its preparation In a number of important processes involving emulsions, *e g*, in the churning of butter, a phase inversion is an essential part of the process It may be said, however, that with a given system of liquids and a single stable emulsifying agent there is practically always one type of emulsion which is much more stable than the other In most cases of phase inversion it can be demonstrated that inversion is accompanied by treatment which either alters the chemical constitution of the emulsifying agent, introduces a second surface active agent, or alters the surface tension of one of the liquids

[9] W D Bancroft *J Phys Chem* **17**, 501–520 (1913) **19**, 275–309 (1915) W D Bancroft and C W Tucker, *ibid*, **31**, 1681 1692 (1927)
[10] G H A Clowes, *J Phys Chem* **20**, 407–450 (1916)

(d) Wetting of Solids

The relationship between the surface tensions of a liquid–solid system and the degree to which the liquid wets the solid have been stated previously, in equations (1) to (7) It is only necessary to add here that any substance is surface active in such a system if its presence alters the degree to which wetting occurs

So called "wetting agents" are the most common liquid–solid surface-active materials These consist of water soluble compounds which are oriented at the surface with the polar heads of the molecules in the water phase and the nonpolar tails toward the solid There are other surface active compounds, however, such as the "collectors" used in ore flotation, whose polar groups are more strongly attracted toward the solid than the liquid Molecules of these compounds assume a reverse orientation at the surface of the solid, and hence decrease the degree to which it is wetted

There are a number of different ways in which surface active agents may alter the characteristics of a liquid–solid system In many applications the function of the surface active agent is merely to promote the spreading of a liquid upon a more or less smooth solid surface, so that the latter may be easily coated with a uniform and adherent liquid film In some cases, as in the use of wetting agents in adhesives, the surface active agent contributes to the strength of the bond between the solid and the liquid In many such instances the liquid is later converted to a solid, so that in effect the wetting agent assists in establishing a bond between two solids

Surface active agents are often important in their effect upon the ease with which a liquid penetrates a mass of fibers, or other porous structure in which capillarity comes strongly into play The driving force which impels a liquid to penetrate a capillary space in a solid material may be expressed by the following equation

$$F = \gamma_{LA} \cos \theta \, x \qquad (8)$$

where F is the force in question, γ_{LA} is the surface tension of the liquid against air, θ is the contact angle of the liquid against the solid, and x is a factor determined by the size of the capillary Wetting agents increase the value of F in the above expression by decreasing the contact angle of the liquid against the solid Dewetting or water-proofing agents decrease the value of F or even cause it to assume a negative value, by increasing the contact angle

Powney,[11] in discussing the penetration of fabrics, has pointed out that the entry of a liquid into very small interstices will be followed by a local

[11] J Powney, in International Society of Leather Trades' Chemists, British Section, *Wetting and Detergency* 2nd ed , Chemical Pub Co , New York, 1939, pp 185–196

impoverishment of its content of surface active molecules, from the relatively great amount of adsorption of the latter on the solid surfaces In the later stages of penetration, therefore, the rate at which diffusion can take place to replenish this impoverishment is important

Certain surface active substances are able to markedly reduce the tendency of solid particles to adhere to one another or flocculate when suspended in a liquid It is considered[12] that these agents function through their ability to form relatively thick adsorbed layers upon the surface of the solid particles Such layers serve to maintain contiguous particles at a sufficient distance to avoid the influence of mutually attractive surface forces Most of the materials which are effective deflocculators contain molecules of relatively large weight and complicated structure Examples of such materials are phosphatides, and oxidized and polymerized glycerides

Surface active agents of the above class not only maintain paint pigments and similar materials in a high degree of dispersion, but may also markedly influence the plasticity or viscosity of suspensions to which they are added The latter effect is fully explainable upon the basis of their influence upon adhesional forces between the solid particles An outstanding example of this phase of surface action is furnished by the use of lecithin to reduce the consistency of chocolate-sugar compositions

The inhibitory effect of low concentrations of certain substances upon crystal formation and growth appears to be explainable upon the basis of adsorption of surface active molecules on the crystal faces The efficacy of lecithin in preventing "bloom" on chocolate surfaces is due to its dispersive effect upon fat crystals Lecithin has also been used as a crystallization inhibitor in winterized cottonseed oil[13] Oxidized, polymerized oils may also inhibit the formation of fat crystals[14]

(e) *Detergency*

The mechanism by which soap and other detergents clean is manifestly complex, and different authorities are by no means in agreement concerning its details However, the principles discussed in the following paragraphs appear to be more or less generally accepted by modern workers in this field, and cover the more important phases of detergent action

In a great many soiled surfaces, the "dirt" is bound to the surface by a thin film of oil or grease The cleaning of such surfaces involves the displacement of this film by the detergent solution, which is in turn washed away by rinse waters

[12] A de Waele, in International Society of Leather Trades' Chemists, British Section, *Wetting and Detergency* 2nd ed Chemical Pub Co, New York 1939, pp 57–66

[13] D P Grettie (to Industrial Patents Corp), U S Pat 2 050 528 (1936)

[14] W Clayton, S Back, R I Johnson, and J F Morse *Nature*, 138, 801 (1936)

The mechanism by which this displacement occurs has been subjected to mathematical analysis by Adam, and the results reported by Robinson[15] It has been demonstrated that the oil film breaks and separates into individual droplets under the influence of the detergent solution In other words, the contact angle of the oil with the solid surface is caused to change from approximately 0° to 180° The oil droplets are, of course, detached from the surface with relative ease by mechanical action

As an expression of the relationship between the above mentioned contact angle, the surface tension and the adhesion tension (a t) in the system, the following equation is presented

$$\cos \theta_{AB} = \frac{\text{(solution–solid a t)} - \text{(oil–solid a t)}}{\text{oil–solution interfacial tension}} \qquad (9)$$

This equation is simply equation (7), restated in semimathematical terms It is to be noted that the angle θ_{AB} in this equation is that made by the oil-solution interface *in the solution* It is, therefore, the supplement of the contact angle of the oil In the process of displacement mentioned above it must change from approximately 180° to 0°

When $\theta_{AB} = 0$, the value of cos θ_{AB} is 1 At higher values of θ_{AB}, cos θ_{AB} is less than 1, or is a negative quantity Therefore, for detergent action to be most efficient, the expression on the right hand side of equation (9) should be as large as possible Detergents contribute to a large value both by increasing the adhesion tension between the solid and the aqueous phase and decreasing the interfacial tension between the aqueous and oily phases

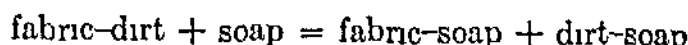
Nonoily dirt is probably removed by a more or less analagous process, *i e*, it is displaced and carried away by the detergent solution through the superior affinity of the latter for the solid surface It has been frequently observed, however, that dirt of any kind is much more difficult to remove from fabrics, etc , in the absence of oil or grease

Emulsification undoubtedly plays a considerable part in detergent action Obviously, if detached oil droplets and dirt particles did *not* become suspended in the detergent solution in a stable and highly dispersed condition, they would be inclined to flocculate or coalesce into aggregates large enough to be redeposited on the cleansed surface In the washing of fabrics and similar materials, small oil droplets or fine, deflocculated dirt particles are more easily carried through interstices in the material than are relatively large ones

It is possible that a significant amount of detergent action may occur through actual solution of oil films in the detergent solution That solutions of soap are capable of dissolving appreciable amounts of organic

[15] C Robinson in International Society of Leather Trades' Chemists, British Section, *Wetting and Detergency* 2nd ed , Chemical Pub Co , New York, 1939, pp 137–151

liquids which are almost insoluble in ordinary water is well known[16] McBain[17] has recently published a detailed discussion of this phase of detergent action, in which he attributes the phenomenon of solubilization to the enclosure of layers of organic liquid within lamellar spaces in large detergent micelles McBain also considers the possible rôle of ion exchange in removing dirt which is derived from an ionizable material The exchange involved is represented as follows



fabric–dirt + soap = fabric–soap + dirt–soap

Hartley[18] does not consider that the solvent action of detergents is important in washing operations conducted in solutions of ordinary detergent concentration However, he admits the probability of it being a major factor in such operations as washing the hands, in which the detergent is applied in a concentrated form

In practice, the washing solution does not often consist simply of the detergent dissolved in pure water Natural waters contain varying amounts of mineral salts and the detergent solution may also contain other electrolytes, either through accident or design The presence of such electrolytes may greatly influence the action of the detergent

In the case of some detergents, such as sodium alkyl sulfates and the Igepons, the presence of dissolved substances may have a pronounced effect upon the surface activity of the detergent The interfacial tension of solutions of these detergents against transformer oil was observed by Robinson[15] to decrease with the addition of electrolytes This effect was independent of the nature of the anion, equimolar solutions of NaCl, NaOH, etc , lowered the interfacial tension to an equal degree The valency of the cation had a large influence, however $LaCl_3$ was more effective than $CaCl_2$, which was in turn more effective than NaCl in decreasing the interfacial tension The influence of the dissolved electrolytes was attributed by Robinson to their probable effect of reducing the mutual repulsion of adsorbed detergent molecules at the interface This would permit closer packing of the latter, with a consequent further lowering of the interfacial tension

The presence of electrolytes also influences the degree to which association of soap molecules occurs in solution Thus McBain, Taylor, and

[16] See for example S U Pickering, *J Chem Soc*, **111**, 86–101 (1917), C R Bailey, *ibid*, **123**, 2579–2590 (1923), E L Smith, *J Phys Chem*, **36**, 1401–1418, 1672 1684 2455–2473 (1932)

[17] James W McBain, in *Advances in Colloid Science*, Vol I Edited by E O Kraemer, Interscience, New York 1942, pp 99–142

[18] G S Hartley, in International Society of Leather Trades' Chemists, British Section, *Wetting and Detergency* 2nd ed , Chemical Pub Co , New York, 1939, pp 153–162

Laing[19] found that the addition of sodium hydroxide increased the concentration of colloidal soap particles at the expense of noncolloidal soap

The reaction of ordinary soaps with hard waters containing soluble calcium and magnesium salts is a matter of common experience It not only produces insoluble curds of calcium and magnesium soaps, which are difficult to remove from fabrics, but also makes the consumption of soap excessive In very hard waters large quantities of soap are required to precipitate these compounds before there is any soap available for detergent action However, most of the synthetic detergents, such as the sodium alkyl sulfates and the Igepons, do not form insoluble compounds with hard waters In some soap products so called "builders," such as sodium silicate, soda ash, or tetrasodium pyrophosphate, are incorporated to serve as water softeners and decrease the amount of soap consumed in softening the water

There are definite limitations to the range of pH within which certain detergents will function Ordinary soap solution will decompose at a pH below about 10, hence must necessarily be alkaline Most of the nonsoap detergents are effective in neutral solution The so-called cation active detergents, in which the major part of the molecule is positively charged, may be used in acid solution

It may be mentioned, finally, that the nature of the surface to be cleaned has some influence upon the relative effectiveness of different detergents This follows from the fact that one of the determining factors in detergent action is the affinity of the detergent solution for the soiled surface, which depends in turn upon the chemical nature of the surface as well as the detergent Thus, for example, the nonsoap detergents are relatively efficient, in comparison with soaps, in washing woolen fabrics or silks, but somewhat less efficient for washing cotton or rayon

3 Applications of Surface-Active Agents

The industrial applications of wetting agents are so many and diverse that no more than a bare outline of the subject can be attempted here As Snell[3] points out in a recent review, "whenever liquid-solid or liquid-liquid interfaces occur, surface activity is a factor," and there is scarcely any process involving the production of such interfaces where surface-active agents are not of present or potential importance

(a) *Detergents*

Much the most important use of surface active agents is as detergents or cleaning materials Tremendous quantities of these materials are required, in homes, in public service institutions, and in industrial plants

[19] J W McBain, M Taylor, and M E Laing, *J Chem Soc*, 121, 621–633 (1922)

Since soap is actually superior to any other class of detergents for many purposes, and is acceptable although not superior for others, and since it is much the cheapest detergent, its use far outweighs that of all other cleaning materials. However, the fact that it cannot be be used except in alkaline solution and that it reacts with hard water, has caused it to be replaced to some extent by other and newer detergents in certain special applications.

There is a certain distinction to be made between the use of detergents in manufacturing plants and in other places, including the home. The principal use of detergents in places of the latter class is to clean clothes, linens, dishes, floors, etc. Detergents which are designed for such use must actually be "all service" materials. Both the dirt and the dirty surfaces may vary widely in character, and the cleaning problems which arise will seldom be definite and clearcut. In manufacturing processes, however, a detergent is usually used to remove a specific substance, usually of an oily nature, from a specific type of surface. In such an application it is possible to select the detergent upon the basis of its ability to perform a particular job. For this reason, the newer, nonsoap detergents have achieved rather greater importance in industrial use than in the household.

(b) *Wetting and Dispersing Agents*

Probably the largest single user of wetting agents is the textile industry, which employs large quantities of sulfonated oils and other materials of the nonsoap variety as textile assistants, to enable dyestuffs to be easily and evenly absorbed by the textile fibers. Wetting agents are also used in mercerization and other chemical finishing treatments applied to textiles, to promote rapid and uniform action on the part of the finishing agent.

Recently, agents which retard wetting, such as metallic salts of the higher saturated fatty acids, have found a considerable use in the manufacture of water repellent fabrics. In treating a fabric for water repellence, as distinguished from waterproofing, the material used for treatment does not form a continuous film within the fabric, but is merely deposited, in relatively small amount, upon the surface of the fibers, where it decreases the wettability of the fabric to such an extent that the pores are not readily penetrated by water droplets. Thus the fabric may retain its original appearance and permeability to air while achieving a considerable degree of waterproofness.

Wetting agents are often added to adhesives to overcome conditions under which an untreated adhesive will be inclined to wet one or the other of the two adhering surfaces insufficiently. Wetting agents may also be used to promote adhesion between solids and other substances which are liquid only at the time at which they are applied to the solids. Examples of solid–solidified liquid systems are dried paint films, oiled fabrics, rubber articles containing textile fibers or fillers, etc.

The most important class of wetting inhibitors consists of the "collectors" used in ore flotation Water to which these substances have been added will completely wet the worthless gangue of ore concentrates, but will only incompletely wet particles of valuable mineral Through the medium of a second surface active agent designed to produce a froth, air bubbles become attached to the unwet surfaces of the mineral particles, carrying the latter away in a floating foam The collectors principally used consist of xanthates and other compounds which are not derived from fatty materials, although there is a considerable use of higher fatty acid amine salts on certain ores

It is common practice to add water soluble wetting agents to insecticide sprays, to improve the spreading and covering properties on plant surfaces, and retention on such surfaces Soaps are used in most sprays, although other surface active agents are required for preparations which contain lime and hence are incompatible with soaps Wetting agents may also improve the effectiveness of insecticides, fungicides, or bactericides which kill upon contact

Wetting agents are often incorporated in polishes and cleaners of the paste type, to enable these materials to make efficient contact with the surfaces to which they are applied They are also of value in the manufacture of cosmetics, inasmuch as the efficiency of many of these products depends upon their wetting or adhesive action

Lubricating oils are improved by the addition of small proportions of certain oil soluble polar compounds These increase the "oiliness" and the film strength of the oil, through the formation of oriented films upon the surfaces of the bearing metal The substances used as addition agents in lubricating oils consist of various esters of monohydric alcohols and chlorinated fatty acids, of which methyl dichlorostearate is particularly preferred Oil soluble wetting agents are also essential constituents of penetrating oils

The surface active agents which are active in paints, varnishes, and enamels and which maintain the pigments of these in a suitably dispersed condition, consist usually of compounds produced *in situ* in the drying oil vehicle, through hydrolysis or oxidation of the drying oil The selection of a drying oil with a high free fatty acid content for pigment grinding is in effect equivalent to the use of a wetting agent, inasmuch as the free acid forms metallic soaps with the pigments However, there is some use of added wetting agents such as alkyl amine and alkyl pyridinium derivatives in pigment grinding The use of such agents has been discussed by Fischer and Jerome[20] In the manufacture of nitrocellulose lacquers the plasticizing agent usually serves as a wetting agent for the pigment but with some nonpolar plasticizers the addition of other wetting agents is desirable

[20] E K Fischer and C W Jerome, *Ind Eng Chem*, 35, 336–343 (1943)

Commercial lecithin is much used as an oil soluble wetting agent in the manufacture of chocolate confections It serves to minimize cohesion between solid particles in the heated chocolate mass, and thus lowers its viscosity, permitting the incorporation of large proportions of sugar It also reduces the tendency to "bloom" on chocolate surfaces through its dispersive effect on solid crystals deposited from the chocolate fat

Among the other uses of materials active at liquid-solid interfaces are for dispersive agents in latex suspensions, as wetting and deflocculating agents in ceramics manufacture, as wetting agents in paper manufacture, as wetting agents in the acid treatment of oil wells, and as wetting agents to prevent the adherence of gas bubbles and consequent pitting in electro plating

(c) *Emulsifying Agents*

In one respect the use of emulsifying agents is essentially different from that of wetting agents Whereas some degree of wetting will usually occur without the benefit of a wetting agent, it is impossible to produce an emul sion without an emulsifying agent An emulsion is a fundamentally un stable system Wetting agents may be said to merely assist the wetting process, in emulsification the emulsifying agent plays a dominant role In some cases emulsifying agents are naturally present in the materials used to produce the emulsion Where they are not present, however, they must be added

There are instances where the production of an oil in water emulsion is merely a means of uniformly distributing a relatively small volume of the oil phase over a relatively large surface Because of the high viscosity of oils, as compared with water, such distribution of an oil alone is difficult Where the emulsion serves merely as an oil carrier, a permanent emulsion is not desired, as the aqueous phase must be removed after it has served its purpose in transporting the oil

The outstanding use of an emulsion to distribute an oil is in the operation of "fat liquoring," as carried out in the leather industry [21 23] In this opera tion wet skins are caused to take up a controlled amount of oil by tumbling in a drum containing the emulsion Since the pH of the water phase may be relatively low, the emulsifying agent most commonly used consists of a sulfonated oil, although soap is sometimes used

Another example of emulsification for the sake of oil distribution is to be found in the so called self polishing floor waxes, which are emulsions of

[21] R M Koppenhoefer, *J Am Leather Chem Assoc*, 36, 118–131 (1942)
[22] R M Koppenhoefer and C E Retzsch, *J Am Leather Chem Assoc*, 35, 78–129 (1940)
[23] J A Wilson, *Chemistry of Leather Manufacture* Vol II, Reinhold New York 1929

waxes in water, stabilized by ethanolamine soaps or other soaps After the emulsion is applied, it breaks down through evaporation of water or ammonia, leaving the wax in the form of a thin, uniform, waterproof film

An important use of emulsifying agents is to produce a highly developed interface between two immiscible phases, for the purpose of promoting a reaction between the two Examples of this application are to be found in the use of reagents of the Twitchell type for promoting fat splitting, and of soap in the polymerization of butadiene for the production of synthetic rubber

Among the popular food products there are a number of emulsions, including butter, margarine, ice cream, and mayonnaise Margarine is relatively lacking in the phosphatide and protein compounds which stabilize butter, hence is frequently fortified with emulsifying agents, to prevent "leaking" while the product is in storage, and spattering during cooking operations Mono- and diglycerides are effective antileaking agents, but do not prevent spattering A related compound, sodium monostearine sulfoacetate, effectively eliminates spattering and is often used for this purpose The addition of mono and diglycerides to ice cream is also claimed to be beneficial, inhibiting the formation of large ice crystals and promoting the incorporation of air in the product

The most important use of synthetic emulsifying agents in the food industry is in the addition of mono and diglycerides to vegetable shortenings, to produce a special fat for cake baking The presence of these materials in the shortening enhances the degree to which it may be dispersed in the cake dough, produces a dough of superior mechanical strength, and hence permits the use of high proportions of sugar and milk

(d) *Foaming Agents*

Much the most important use of foaming agents, as explained previously, is in ore flotation Other important examples of useful or desirable foams include those produced by certain types of fire fighting equipment, and the foam in beer Surface active agents are used in producing fire extinguishing foams and also to some extent in beer Surface active agents may also in certain instances be employed to inhibit foaming [24]

4 Soaps

Strictly speaking the term "soap" refers to all salts of the fatty acids of higher molecular weight In the present discussion, however, consideration will be given only to those soaps which are soluble in water and hence have well developed surface active properties Soaps of the alkaline earths or the heavy metals, which are of service in lubricating greases and other

[24] For a discussion of foam inhibitors and the theory of foam inhibition, see S Ross and J W McBain, *Ind Eng Chem*, 36, 570–573 (1944)

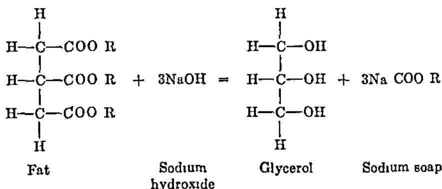
compositions but do not form surface active solutions, will be discussed in another chapter The soluble soaps consist chiefly of sodium and potassium compounds, but also include ammonia and amine soaps

The soap industry is the second largest consumer of fats and oils, being outranked only by the food industry The per capita consumption of soap in different parts of the world varies extremely In the United States it amounts to approximately 25 pounds yearly, but in most European countries it is much less than this, and in some portions of the globe it is negligibly small

Soap is consumed in a number of different forms In the United States by far the greatest part of the soap produced is in a solid form and is marketed either in bars or in flakes, chips, etc In Europe, however, where the animal fats which produce hard soaps are not so generally available, the use of liquid soaps is much more common

(a) Nature of the Soapmaking Process

In its simplest terms, soapmaking consists of reacting an alkali solution with a fat or oil to produce soap and glycerol.



The consistency, solubility, and other properties of the finished soap depend to some extent upon the nature of the fatty acids involved in the reaction, as will be explained in a later paragraph To a larger degree, however, the properties of the soap are dependent upon the alkali used in its manufacture Sodium soaps, which are relatively firm, are termed in the soap trade "hard" soaps Potassium soaps, which are soft or even liquid, are termed "soft" soaps

Some soaps are made by the "cold made" or "semiboiled" processes, in which there is no separation of the products of reaction after the process is completed, so that the glycerol remains in the soap The more commonly employed process, however, is the "full boiled" process, in which saponification is carried out in a series of successive stages, the soap being salted out from the glycerol solution and the latter drawn off after each stage This method of saponification not only permits recovery of most

of the valuable glycerol, but also results in the removal of a certain proportion of the coloring materials and other impurities in the fat, with consequent improvement in the quality and appearance of the soap

There is also a certain amount of soap produced by the action of caustic soda or soda ash on fatty acids These acids may be obtained from the acidulation of "foots" from the alkali refining process, or from the splitting of fats by the Twitchell or autoclave methods Such soap is, of course, entirely free from glycerol

The term "soap" as used here does not refer to anhydrous soap, but rather to the physicochemically complex system of soap and water which is

TABLE 117
PRODUCTION OF SOAP IN THE U S IN 1929 AND 1939[a]

Type	Production million lbs	
	1939	1929
Toilet soap (bars)	409	324
White laundry soap (bars)	661	915
Yellow laundry soap (bars)	579	551
Granulated powdered and sprayed soaps	893	337
Soap chips and flakes (packaged)	284	388
Soap chips and flakes (bulk)	134	
Washing powder (packaged)	132	506
Washing powder (bulk)	110	
Cleansers scouring powders (packaged)	167	
Cl ansers scouring powders (bulk)	19	
[illegible]	5 6	11 1
[illegible]	7 9	
[illegible]	42 8	35 2
[illegible]	62 5	—
[illegible] id liquid	31 0	—

[a] U S Bur Census *Census of Manufactures*, 1939 Washington 1940

produced by the various soapmaking processes and marketed under the simple designation of "soap " Such soap actually contains from about 5% to 35% water

Aside from the nature of the raw materials and the different methods of effecting saponification mentioned above, the character of a soap product is considerably affected by the physical methods employed in converting it to the form in which it is finally to be marketed and used The molten soap from the soap kettle may be simply run into frames and allowed to cool to a solid form in large masses, which are later cut up and pressed into bars or it may be solidified in flakes or "chips," which are formed into bars of quite different characteristics by the operations of milling, plodding, and pressing It may also be marketed in the form of chips or flakes, or

spray-dried in granules, beads, etc, with or without the admixture of soda ash, sodium silicate, sodium phosphates, or other "builders"

(b) *Physicochemical Nature of Soaps*

The sodium and potassium soaps of the common fatty acids are capable of existence in a remarkable variety of forms The soap-water phases represented by niger, neat soap, and soap curd have been recognized since the beginnings of the soap boiling art However, our knowledge of the true nature of these and other aqueous soap phases dates from the work of Maclennan,[25] which was reported in 1923

By the microscopic examination of samples with the aid of polarized light, Maclennan demonstrated that neat soap belongs to the class of anisotropic or crystalline liquids, that niger is an ordinary isotropic solution, devoid of crystalline structure, and that soap curd and ordinary finished soap consist of a heterogeneous mass of solid, fibrous crystals enmeshing a liquid phase Thus he established the existence of three distinct phases isotropic soap solution, neat soap, and curd fibers Later, McBain and Langdon[26] distinguished a second, more dilute liquid crystalline phase, which was termed "middle soap" Recently Vold[27] has produced experimental evidence which suggests the existence of a third liquid crystalline phase, "superneat soap", and McBain and co workers[27a] have detected a new waxlike phase which they have termed "kettle wax"

Anhydrous soaps exhibit an even greater variety of phases The researches of Ferguson and associates,[28] later extended by Vold and co workers,[29,30] have revealed that a single pure anhydrous soap may pass through at least seven successive phases as it is heated from ordinary room temperature to the point where it becomes a completely isotropic liquid In the case of sodium palmitate the different forms are curd fiber, to 117°C, subwaxy, to 135°, waxy, to 172°, superwaxy, to 208°, subneat, to 253°, neat, to 295°, and isotropic liquid, above 295° The term "neat soap" refers here simply to the form which first appears upon cooling the isotropic liquid, and has no necessary identity with "soap boiler's neat soap" There is some evidence that there may be other phases, as yet undefined, within the lower range of temperatures

The change from one phase to another contiguous phase is in every

[25] K. Maclennan, *J Soc Chem Ind*, **42**, 393–401T (1923)
[26] J W McBain and G M Langdon, *J Chem Soc*, **127**, 852–870 (1925)
[27] R D Vold, *Soap*, **16**, No 6, 27–30 (1940)
[27a] J W McBain, R C Thorburn, and C G McGee, *Oil & Soap*, **21**, 227 230 (1944), J W McBain, K Gardiner, and R D Vold, *Ind Eng Chem*, **36**, 808–810 (1944)
[28] R H Ferguson, R D Vold, and F B Rosevear, *Oil & Soap*, **16**, 48–51 (1939)
[29] M J Vold, M Macomber, and R D Vold, *J Am Chem Soc*, **63**, 168–175 (1941)
[30] R D Vold and M J Vold, *J Am Chem Soc*, **61**, 808–816 (1939)

case completely reversible, both in the anhydrous soaps and in the aqueous phases. Consequently, as has been shown by McBain,[31] soap–water systems are in every way amenable to Gibb's phase rule. The application of phase diagrams has done much to establish the soap boiling process on a scientific basis.

The fact that commercial soaps are mixtures of the soaps of a number of different fatty acids does not invalidate the application of phase rule diagrams to these materials. Within the regions with which the soap boiler is concerned there is no appreciable fractionation of the different soaps in transition from one phase to another. Practically speaking, a commercial soap may be said to behave similarly to the soap of a single pure fatty acid.[26,32,34]

Phase diagrams for aqueous systems of sodium laurate, sodium myristate, sodium palmitate, sodium stearate, sodium oleate, and a commercial toilet soap have been constructed over a period of years by McBain and his associates. Recently a revised set of diagrams for all of these systems has been prepared from the best available data and presented by McBain and Lee.[35] Their diagrams for sodium oleate and commercial soap are reproduced in Figures 40 and 41. It is to be noted that these diagrams are in some regions incomplete. In other regions the boundaries have been only tentatively placed, and hence are indicated by dotted rather than continuous lines. The typical behavior of aqueous soap systems may be deduced from the diagrams.

The two diagrams are divided into areas within which soap–water exists as a single phase, and other areas in which two contiguous phases are present in an equilibrium mixture. Tie lines drawn across the latter areas are necessarily horizontal, since they represent equilibria under isothermal conditions. The tie lines, which are drawn in the diagrams at regular intervals, give the areas of heterogeneity a shaded appearance, whereas the areas within which there is a single phase are unshaded.

In Figure 40 the transition points of the various anhydrous phases of sodium oleate are indicated along the left vertical axis of the diagram. Sodium oleate appears to differ from corresponding soaps of the saturated fatty acids in exhibiting no anhydrous neat phase. However, the curd, subwaxy, waxy, superwaxy, and subneat forms can be distinguished, as well as the isotropic phase. With the addition of a small percentage of water the anhydrous phases are brought a short distance within the hydrous region, in the form of "tongues" which are inclined sharply downward. Thus the presence of even a very small amount of water serves to markedly

[31] J. M. McBain in *Colloid Chemistry*, Vol. I. Edited by J. Alexander, Chemical Catalog Co., New York, 1926, pp. 137–164.

[32] R. H. Ferguson and A. S. Richardson, *Ind. Eng. Chem.*, 24, 1329–1336 (1932).

[33] R. H. Ferguson. *Oil & Soap* 9, 5–8, 25 (1932).

[34] J. W. McBain, M. J. Vold and J. L. Porter, *Ind. Eng. Chem.*, 33, 1049–1055 (1941).

[35] J. W. McBain and W. W. Lee, *Oil & Soap*, 20, 17–25 (1943).

lower the transition points of the various anhydrous phases With the further addition of water the anhydrous phases soon disappear and the distinctive aqueous phases make their appearance In Figure 41 it will be noted that the transition from one anhydrous phase to another is not abrupt, but occurs over a range of temperatures Thus in the case of commercial soaps there is in these phases some fractionation of the various individual components during transition

By following the 100°C isotherm across Figure 40 from right to left it will be seen that sodium oleate assumes the following successive forms as its

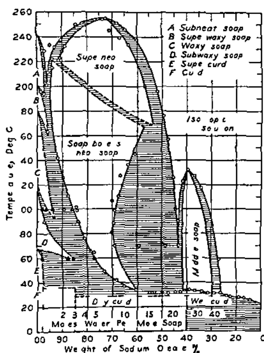


FIG 40 —Phase diagram of the system sodium oleate-water [35]

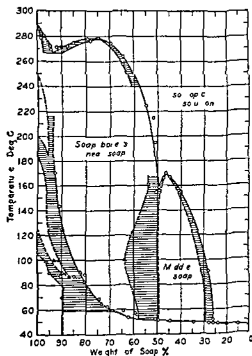


FIG 41 —Phase diagram of a commercial toilet soap and water [35]

concentration in water at this temperature is increased from 0–100% from 0–31%, isotropic solution, 31–34%, isotropic solution and middle soap, 34–42% middle soap, 42–43%, middle soap and isotropic solution, 43–44%, isotropic solution, 44–69% isotropic solution and soap boiler's neat soap, 69–86%, soap boiler's neat soap, 86–94%, soap boiler's neat soap and waxy soap, 94–96%, waxy soap, 96–98%, waxy and subwaxy soap, 98–100%, subwaxy soap

Similarly, the toilet soap (Fig 41) at 100°C is in the form of an isotropic solution from 0–29% concentration, between 29% and 32% it is heterogeneous and consists of isotropic solution and middle soap, from 32–49% it consists solely of middle soap, from 49–64% it is again heterogeneous,

consisting of middle soap and soap boiler's neat soap, from 64–85% it consists entirely of soap boiler's neat soap, etc

In a similar manner it is possible to trace the composition of a soap of given concentration as its temperature is varied If, for example, a line representing 65% soap is traced vertically from the bottom to the top of Figure 40, it will be seen that a sodium oleate soap of this composition assumes the following forms as it is heated from ordinary room temperature to complete melting to 32°C, curd fiber and isotropic liquid, 32–34°, curd fiber and middle soap, 34–36°, curd fiber and soap boiler's neat soap, 36–54°, soap boiler's neat soap, 54–70°, soap boiler's neat soap and middle soap, 70–130°, neat soap and isotropic solution, 130–175°, soap boiler's neat soap, 175–180°, soap boiler's neat soap and superneat soap, 180–240°, superneat soap, 240–249°, superneat soap and isotropic solution, above 249°, isotropic solution

The various soap phases differ somewhat in consistency and gross appearance In the case of sodium palmitate, the anhydrous phases have been described by Vold[27] as follows curd fiber phase, a hard, opaque white solid, subwaxy phase, slightly less opaque and less hard than the curd fiber phase, waxy and superwaxy phases, similar in appearance to subwaxy, but progressively softer, subneat phase, translucent and much less viscous than the waxy phases, flowing under its own weight, neat phase, similar to the subneat phase, but less chalky, isotropic liquid, clear and relatively low in viscosity, permitting entrained air bubbles to readily escape

The aqueous phases of sodium oleate are described by the same author as follows middle soap, nearly transparent and very stiff, does not flow in 12 mm tubes, soap boiler's neat soap, rather turbid and translucent, fairly fluid, superneat soap, very similar to soap boiler's neat soap, perhaps slightly clearer The anhydrous phases are very little changed in appearance as they are extended into the hydrous region Isotropic soap solution is, of course, relatively clear and fluid

At ordinary atmospheric temperatures sodium soaps of high moisture content consist of a heterogeneous mixture of the curd fiber phase and isotropic liquid The crystal phase may contain water, and a large number of different hydrates have been reported for pure soaps However, the recent work of Ferguson and associates[36] makes it appear doubtful that most of these are definite compounds

McBain and co workers[34, 35] have pointed out the significance of point T_s, at the lower left corner of the field of isotropic solution The temperature represented by this point is termed the "temperature of ready solubility," since here the boundary between isotropic solution and curd fiber-isotropic solution is nearly horizontal and a slight change in the temperature is accompanied by a very large change in solubility In the case of

[36] R H Ferguson, *Oil & Soap*, 21, 6–9 (1944)

nated alpha and beta, was recognized by Thiessen and co workers[45,46] The existence of a third, omega, form was revealed in patents issued to Mills[47] More recently a fourth form, designated as delta, has been described by Ferguson, Rosevear, and Stillman[48] The latter authors present conclusive x ray diffraction evidence for the existence of the four forms, and in addition discuss in some detail the properties of solid commercial soaps in relation to their content of the various crystal phases

The alpha form of sodium soaps, which is in reality a slightly hydrated phase, reverting to the beta phase on complete dehydration, does not appear to exist within the range of conditions ordinarily encountered in commercial soaps However, the beta, omega, and delta forms are all encountered in commercial soaps They are often somewhat mixed, although many soaps may be prepared in forms consisting substantially of any one of the three according to the conditions accompanying transformation of the soap to a solid form

The temperature ranges within which the three forms are stable do not appear to be clearcut and distinct, but in general they may be said to increase in the order, delta, beta, omega Spontaneous transformation of one form to another, in the above order, readily takes place with increase in temperature As the soap is cooled, however, transformations in the opposite direction occur more reluctantly In some cases spontaneous transformation does not occur so long as the soap remains in a static condition Milling, plodding, mixing, extrusion, or other mechanical working of the material will initiate phase transformation, however, and can generally be depended upon to produce the soap substantially in the form which is stable under the conditions of working

In framed soaps, which are solidified without agitation, the omega phase is the one chiefly obtained On the other hand, the beta form is the predominant form in milled soaps, conversion from the omega form being produced by milling and plodding Beta form soaps may be produced without milling, however, by quickly chilling neat soap below a critical temperature at which this form becomes stable, and then agitating the partially solidified mass to effect the desired conversion from the omega to the beta form[47] The critical temperature for any soap varies with both its fatty acid composition and its moisture content In the case of 20% coconut oil–80% tallow soap of 26% moisture content it is stated to be about 160°F[47] In soap of lower moisture content, it is higher Soaps of low

[45] P A Thiessen, J von Kleck, H Gockowiack and J Stauff, *Z physik Chem*, A174, 335–358 (1935)

[46] P A Thiessen and J Stauff, *Z physik Chem*, A176, 397–429 (1936), A177, 398 (1936)

[47] V Mills (to Procter and Gamble Co) U S Pats 2 295 591 96 (1942)

[48] R H Ferguson, F B Rosevear, and R C Stillman, *Ind Eng Chem*, 35, 1005–1012 (1943)

molecular weight, such as those made exclusively from coconut oil either do not transform to the beta phase or transform with extreme slowness Formation of the omega phase, therefore, is favored by high temperatures, low moisture content, and low molecular weight of the soaps Transformation of the omega to the beta phase is accomplished by agitating the soap in the range of temperature and moisture content within which the latter phase is stable In the case of neat soap, conversion to the beta form must proceed in this manner through the omega phase Systems of higher moisture content may in some cases produce the beta or even the delta phase upon being cooled without agitation

The delta phase, in contradistinction to the omega phase, tends to be formed under the conditions of low temperature, high water content, and high molecular weight in the soaps It appears in soaps of high water content upon cooling and is produced by milling or otherwise working beta phase soaps at low temperatures, *e g*, 50–60°F Pure coconut oil soaps do not appear to form the delta phase

Beta phase soap is chiefly distinguished from omega phase soap by its property of readily swelling and softening in water Hence, when it is rubbed with a wet sponge, brush, etc , or agitated in the flake or bead form with water, it lathers more readily than omega soap It is also slightly firmer than omega soap Delta soap is intermediate between beta and omega soap in ease of lathering, but is much softer than either of the other two modifications

TABLE 119
PROPERTIES OF THREE PHASES OF A TYPICAL COMMERCIAL SOAP[a]

Property	Beta	Omega	Delta
Firmness arbitrary units	8 0	7 2	3 0
Per cent soap rubbed off bar in use in water[b]	2 4	0 5	1 7
Reaction to water when soaked	Swells and disintegrates	No swelling or disintegrating	Cracks with little swelling

[a] R H Ferguson F B Rosevear and R C Stillman *Ind Eng Chem* 35 1005-1012 (1943)
[b] This figure is a measure of the ease of lathering of the bar of soap

The comparative properties of soaps of the three different forms are indicated in Table 119 which is taken from the publication of Ferguson, Rosevear, and Stillman[48] Each of the three soaps mentioned in this table were prepared from the same 20% coconut oil–80% tallow batch The sample in the beta phase was converted to this form by the operations of milling and plodding The omega soap was prepared from a bar of the milled soap by heating the latter to 190°F in a sealed container and allowing it to cool quietly to room temperature The delta sample was prepared by reworking the milled soap at 50–60°F

In addition to its effect on the crystal modification existing in the soap, mechanical working, as in milling, extrusion, etc , hardens the soap and renders it less opaque, through its tendency to produce orientation and compacting of the fibers In this respect milling is somewhat more effective than extrusion without milling Extruded soap bars are said to be 10% more soluble on the side faces than on the end faces, through orientation of soap fibers [47]

Many physicochemical investigations have been concerned with the manner in which soaps and other surface active materials dissociate, associate, or hydrolyze in aqueous solution

The early work of McBain and others rendered it apparent that there is some species of ionic aggregation in soap solutions In general, the electrical conductivity of soap solutions is much greater than is to be expected from their content of crystalloid material, as indicated by osmotic or freezing point methods This would suggest the presence of particles carrying a multiplicity of electrical charges The transport number data furnish further evidence of ionic association As the concentration of the solutions is increased, migration of the fatty acid radical increases abnormally, indicating the formation of ionic aggregates of high mobility

There are certain peculiarities in the manner in which the equivalent conductivity of soap and other detergent solutions changes with concentration of the solution Very dilute solutions behave not very differently from ordinary electrolytes, with the conductivity decreasing normally with increase in concentration At a certain critical concentration, however, the conductivity begins to decrease very rapidly with increasing concentration of the solution, and thereafter it passes through a minimum, and then slowly increases

According to the theories of Hartley,[49] the point of rapidly decreasing conductivity is that at which associated ions or ionic micelles begin to appear in the solution On the other hand, it is McBain's view that ionic micelles appear at a higher concentration, corresponding to the point of minimum equivalent conductivity In order to explain all the observed effects, McBain postulates the existence of large lamellar micelles in which water is enclosed between alternate layers of neutral, oriented soap molecules Thus soap solutions are conceived to consist of systems in which simple electrolyte, ionic micelles, and neutral colloidal particles are all present The three forms are in equilibrium, and the electrical behavior of the solution is determined by the relative proportions of the three, which depends in turn upon the nature of the soap, the temperature and concentration of the solution, and the extent to which foreign electrolytes are present

[49] G S Hartley *Kolloid Z* , 88, 22–40 (1939)

The mobile and highly charged ionic micelles are considered to be of approximately spherical form, and to consist of a group of fatty acid chains oriented toward a common center From the results of ultrafiltration experiments McBain and Jenkins[50] concluded that their diameter is between 9 and 15 mμ A diameter of the same order of magnitude is suggested by Hartley,[49] i e approximately twice the length of a single fatty acid chain McBain and Jenkins estimated the dimensions of the neutral micelles to be of the order of 75 to 450 mμ

McBain's concept of neutral lamellar micelles is rejected by Hartley, who advances the alternative hypothesis of small cations or "gegenions" which may become adherent to the surface of the ionic micelles Such attached, oppositely charged ions would partially neutralize the ionic micelles Their attachment or detachment with changing conditions in the solution would have the same electrical effect as a shift in equilibrium among the three solute forms suggested by McBain

The exact nature of the particles present in soap solutions can thus hardly be regarded as settled A number of recent workers in the field appear to generally favor the views of Hartley However, it has been pointed out by McBain[17, 51] that recent x ray evidence strongly supports his theory of lamellar micelles

It was once believed that the free alkali formed as the result of hydrolysis in soap solutions played a major role in detergent action However, the work of McBain and Martin[52] showed that extensive hydrolysis did not occur, and that the detergent action of soap must be largely physical in nature McBain and Martin concluded that hydrolysis produced only acid soaps of very low solubility and poor detergent properties

Late investigations[53] have produced data to considerably modify Mc Bain's original conclusions Whereas it was formerly assumed that only simple ions were hydrolyzed, and that acid soaps were produced by secondary reaction, it is now postulated by Ekwall[54] that there is stepwise association in the solution according to the concentration of the latter, and that the association products hydrolyze directly, to yield a variety of hydrolysis products Hydrolysis occurs more readily as association increases The course of hydrolysis of a sodium laurate solution at 20°C is represented by Ekwall and Lindblad[55] to be as follows At the highest dilutions, the degree

[50] J W McBain and W J Jenkins *J Chem Soc* **121**, 2325–2344 (1922) See also J Stauff, *Kolloid Z* , **96**, 244–251 (1941)

[51] J W McBain, *Nature*, **145**, 702–703 (1940)

[52] J W McBain and H E Martin, *J Chem Soc* , **105**, 957–977 (1914)

[53] P Ekwall *Kolloid Z* , **77**, 320–323 (1936), **80**, 77–100 (1937), **85**, 16–24 (1938), **92**, 141–157 (1940) J Powney and D O Jordan, *Trans Faraday Soc* , **34**, 363 367 (1938) J Stauff, *Z physik Chem* , **A183**, 55–85 (1938), **A185**, 45–59 (1939)

[54] P Ekwall, *Kolloid Z* **92**, 141–157 (1940)

[55] P Ekwall and L G Lindblad, *Kolloid-Z* , **94**, 42 57 (1941)

of hydrolysis decreases normally as the concentration increases Below a limiting concentration of about 0 006 N, hydrolysis produces two univalent ions, and forms free lauric acid When the solution becomes saturated with lauric acid, and this acid begins to separate, the degree of hydrolysis becomes constant Immediately above the limiting concentration, hydrolysis produces double ions of the relatively insoluble acid soap, *NaLHL* At a concentration of about 0 0075 N, crystals of the insoluble acid soap begin to separate, and at the same time the degree of hydrolysis begins to rise Hydrolysis at this point appears to produce triple ions of a soluble crystalline liquid acid soap At a concentration between 0 021 and 0 022 N, quadruple laurate ions begin to be produced, from acid soaps of the formula 3 NaLHL, and the degree of hydrolysis again increases Beyond a normality of 0 03, there is further association and increase in the degree of hydrolysis, and it is only at a normality of about 0 06 that the degree of hydrolysis finally begins to fall off

Powney and Addison[56] have noted breaks in the curves representing surface tension *vs* concentration in aqueous soap solutions, due to stepwise association, and similar breaks have been recorded by Phillippoff[57] in curves of viscosity *vs* concentration

(c) *Raw Materials for Soapmaking*

The oils and fats which serve as raw materials for the manufacture of soaps are to be considered principally from the standpoint of their fatty acids composition Glyceride structure is of no consequence in soap makers' fats The natural antioxidants which are such important constituents of edible oils and fats are probably to some extent lost in the saponification process, and in any event a wide variety of artificial antioxidant materials are available for addition to soaps, since antioxidants for soaps are not required to be edible The coloring materials present in fats are of some consequence, inasmuch as they are partially carried into the finished soap Colored substances may be eliminated entirely from even extremely dark fats by splitting the fats and distilling and using only their fatty acids, but this of course entails considerable expense

Aside from fats, the only saponifiable material used to any extent in soap is rosin This material was heavily depended upon at one time by United States soapmakers, but its use has declined, and in late years the total amount consumed has not amounted to more than about 5% of the consumption of fats

In the case of soaps made experimentally from single fatty acids, both the surface active properties of the soap and its solubility will be found to be highly dependent upon the length of the fatty acid chain and its degree of

[56] J Powney and C C Addison, *Trans Faraday Soc*, 33, 1243 1253 (1937)
[57] W Phillippoff, *Kolloid Z*, 96, 255–261 (1941)

unsaturation It is not surprising therefore, that the fatty acids which may be regarded as really desirable materials for sodium soap manufacture are quite restricted in number Specifically, they consist of the saturated acids with 12 to 18 carbon atoms, i e , lauric, myristic, palmitic and stearic acids, and oleic acid Acids with less than 12 carbon atoms are insufficiently high in molecular weight to possess good surface activity, and acids containing more than 18 carbon atoms are too nearly insoluble in water at ordinary temperatures to be useful Sod um oleate has good detergent properties, comparable to those of sodium stearate It has the advantage over sodium stearate of being much more soluble at ordinary temperatures and the disadvantage of being unsaturated and hence somewhat susceptible to oxidation However, linoleic, linolenic, and other more unsaturated fatty acids, produce soft soaps which not only are easily oxidized, but are also relatively poor detergents, presumably because a multiplicity of double bonds in the fatty acid chain interferes with proper surface orientation of the soap molecules Neither ricinoleic acid nor the iso oleic acids produced by hydrogenation is considered desirable in soaps

Unsaturated acids produce soaps which are inclined to be somewhat sticky, and which give an undesirably "greasy" lather

Soaps made from the higher fatty acids (*e g* , stearic) are very efficient detergents However, the fact that they are soluble but to a limited extent in cold or warm water limits their usefulness as ordinary household soaps Soaps of the lower fatty acids (*e g* , lauric acid) are freely soluble and yield a profuse, if somewhat unstable lather However, they are less efficient in their detergent action than soaps of higher fatty acids Although they lather readily from a bar or other solid form, their sudsing properties in solution are relatively poor In practice, a soap actually has two functions, *i e* a certain portion of it must serve as a water softener before the remainder can function as a detergent Considerably larger quantities of lower molecular weight soaps are required for a given degree of water softening, as compared with soaps of high molecular weight

The optimum balance between high solubility and free lathering on one hand, and lasting lather and good sudsing, with high detergent activity and good water softening capacity on the other, is probably attained in soaps of myristic (C_{14}) acid Unfortunately, no fat containing a high percentage of this acid is available in large quantities In practice, therefore, the above mentioned balance is obtained by using fats which yield a proper mixture of lauric, palmitic, stearic, and oleic acids, with other acids of course being present in minor proportions Thus the standard fat mixture for the production of the higher grade household soaps has for many years consisted of tallow, palm oil, hydrogenated marine oils and other fats of high molecu lar weight mixed with 15% to 30% of coconut or palm kernel oil

Under ordinary conditions, both coconut and other free-lathering oils,

and tallow and other slow-lathering oils are available in quantities sufficient to maintain the proper balance between the two classes of ingredients In the absence of a free supply of coconut-type oils, soapmakers may incorporate considerable amounts of potassium soaps into their products The use of a moderate amount of potassium soap in a product made from tallow or similar fats has the effect of solubilizing it and to some extent conferring upon it the properties of a tallow–coconut oil soap, without making it markedly softer

TABLE 120

FATS OILS, AND ROSIN USED IN THE MANUFACTURE OF SOAP IN THE U S (1941)[a]

Item	Quantity 1000 lbs
Tallow, inedible	1,057,303
Whale and fish oils	76 312
Grease	310,487
Palm oil	129,871
Tallow edible	4,826
Oleostearine	70
Lard	89
Coconut oil	484 124
Palm kernel oil	1,113
Babassu oil	29,753
Cottonseed oil foots and other foots	166,000
Olive oil, foots, and inedible	10,584
Soybean oil	24,737
Cottonseed oil	3,010
Corn oil	4,948
Castor oil	1,976
Linseed oil	2,278
Peanut oil	597
Sesame oil	304
Oleo oil	189
Rape oil	5
Olive oil, edible	84
Neats foot oil	35
Perilla oil	—
Tung oil	—
Sunflower oil	—
Other oils	1,162
Total fats and oils	2,309,857
Rosin	125,684
Total saponifiable materials	2,435,541

[a] U S Dept Agr , *Agricultural Statistics*, Washington, 1942

The fats and oils used in soap manufacture are in general low grade products, which sell at prices substantially below those commanded by edible animal fats, drying oils, or the more choice nondrying vegetable oils Up to the present time there has been only a very minor consumption in soap manufacture of lard, edible olive oil, cottonseed oil, peanut oil, soybean oil, linseed oil, or any other oil or fat held in the highest esteem for edible use or for paint manufacture

The amounts of the various fats and oils consumed in the manufacture of soap in the United States in a recent year are listed in Table 120 It

will be noted that of 2,310,000,000 pounds of fats consumed, 1,368,000,000 pounds, or 59% consisted of inedible animal fats, *i e* tallow and grease About half the remainder, or 20%, consisted of coconut oil European soapmakers are accustomed to using lesser proportions of animal fats and correspondingly greater proportions of vegetable oils In Great Britain the vegetable oils used consist chiefly of palm oil, palm kernel oil, hydrogenated whale oil, and other fats which produce hard soaps, but in other European countries there is a considerable consumption of soft vegetable oils

Tallow has long been the basic ingredient of the soap made in the United States Tallow soap is firm, has good keeping qualities, and is an efficient cleaning material Tallow is used as the sole fat in the manufacture of bulk chips for use by commercial laundries but in most other soap products it is mixed with coconut oil, in order to improve the solubility and lathering properties of the soap It must be refined and more or less drastically bleached before it is charged to the soap kettle, but is not ordinarily subjected to other treatment

Greases are less desirable soap fats than tallow They are higher in iodine value and consequently produce a softer soap with poorer keeping qualities They are often subjected to slight hydrogenation, to make them more closely resemble tallow before use The darker grades, like tallow, are bleached and very low grade greases, such as garbage or extraction greases are often split and their fatty acids distilled for use in soap

Whale and fish oils are invariably hydrogenated, to the approximate consistency of hard tallow, before they are used in soaps However, fish oil which has been sufficiently hardened to eliminate permanently its objectionable odor produces a soap which is even less soluble than tallow soap It is consequently blended with softer oils or coconut oil, or both, for soap making purposes

Soap prepared exclusively from palm oil is said to be inclined to be somewhat hard and crumbly, hence is customarily mixed with coconut oil soap, either alone or in combination with soap from tallow or softer fats or oils Although the very dark orange red color of palm oil may be bleached by suitable methods it is difficult to prepare a very white soap containing a large percentage of this oil

Because of its high content of lauric acid, coconut oil is ordinarily considered an essential ingredient of toilet soaps, packaged flakes, beads, etc , and other products in which ready solubility and good lathering are important Palm kernel oil and babassu oil, cohune oil and other kernel oils of American palms are similar in fatty acid composition to coconut oil, and confer the same properties upon the soaps in which they are used Palm kernel oil has never been widely used in the United States, but in Europe its use is rather more common than that of coconut oil The Amer-

ican palm kernel oils have recently become a considerable factor in soap production in the United States

Oils of the coconut type are not ordinarily used alone except in the manu facture of special soaps for use with very hard water or sea water, in which lathering ability is all important

Coconut oil soap is ordinarily very white, is extremely resistant to oxida tion, and is firm in consistency The presence of this oil in high grade milled toilet soaps is considered to contribute to the polished appearance which is desired in the finished bars

In the United States the various liquid oils, such as olive oil cottonseed oil, peanut oil, corn oil, soybean oil, etc , may be classed as very minor contributors to the soap kettle The greatest portion of these oils is con sumed in the form of foots or acidulated foots from the alkali refining of cottonseed and soybean oils The foots are a by product of the refining of these oils for edible purposes and are consumed in soap merely because they are unsuitable for most other purposes They go largely into the manufacture of low grade washing powders, cleansers, etc

In some products, notably the liquid potash soaps used for washing auto mobiles and painted and linoleum surfaces, a drying or semidrying oil such as linseed, soybean or corn oil is a desirable ingredient

Rosin, which is composed substantially of abietic acid, is generally con sidered an inferior soapmaking material, although it is a valuable softening and solubilizing agent Rosin soaps are distinctively yellow in color and soaps containing too great a percentage of rosin are inclined to be soft and sticky Rosin is principally used in the manufacture of yellow laundry soaps

Besides the saponifiable materials mentioned above, the most important raw material used by soapmakers is caustic soda Soda ash will not saponify glycerides, but is used to some extent in saponifying fatty acids and is also used in large quantities as a builder in laundry soaps of all forms Caustic potash is employed almost exclusively in making soft soaps, although potassium carbonate, like sodium carbonate, may be used to saponify fatty acids It is important for the alkalies used for saponi fication to be as free as possible from iron or other heavy metals as these may cause the soap to discolor, and some have a deleterious effect upon the resistance of the soap to oxidation

An important class of laundry soap constituents is comprised of the so called soap builders These consist of certain sodium salts of weak in organic acids, which are alkaline in solution The most commonly em ployed builders are soda ash, the various sodium silicates, trisodium phosphate, tetrasodium pyrophosphate, and sodium hexametaphosphate The builders are less expensive than soap, hence in some cases are used merely in order to cheapen the product In other cases, however, they have

a highly important function, inasmuch as they contribute considerably to economies in soap consumption They serve in place of the more expensive soap to neutralize the natural acidity of certain soiled materials, particularly soiled clothes, and also function as water softeners Tetrasodium pyrophosphate is particularly effective in the latter capacity[58] It is capable of more or less completely eliminating magnesium hardness in water, through the formation of a soluble complex with magnesium ions and is also to some extent similarly effective with calcium It is now a more or less standard ingredient of the popular brands of packaged soap granules Sodium hexametaphosphate is an even more effective water softener than tetrasodium pyrophosphate, particularly in waters high in calcium salts, but is rather too expensive for ordinary use

Salt is an essential material in soapmaking, but no significant amount ordinarily remains in the finished soap

Certain compounds which may be incorporated into soaps are important from the standpoint of their antioxidant effect, or ability to stabilize the soap against rancidity An excess of alkali of any kind appears to exercise some measure of antioxygenic activity Sodium silicate is a well known antioxidant Sodium hyposulfite and sodium thiosulfate are sometimes added to soaps in small amounts purely for their antioxidant value Stannous chloride is a powerful antioxidant and also is useful in white soaps as a bleaching agent Rosin is to some degree an antioxidant

Titanium dioxide is often incorporated in white milled soaps to improve the whiteness of the product, as is also zinc oxide Siliceous materials are used as abrasive agents in scouring soaps and powders and mechanic's hand soaps

Perfumes are an invariable ingredient of toilet soaps, and many of these soaps are also artificially colored A considerable variety of other materials are used to convey distinctive properties to special toilet soaps including alcohol, sugar, pine tar oil, cresol, pyrethrum or derris extractives, sulfur, mercury salts, etc

Organic solvents such as petroleum naphtha and cyclohexanol are sometimes added in minor amounts to laundry and industrial soaps for their solvent and dispersive action

(d) *Characteristics of Soap Saponified by Different Methods*

The full boiled process is commonly used for saponifying fats, because it recovers the glycerol produced by saponification, and also produces pure and high grade soaps Properly carried out, this process gives a product completely free of unsaponified fat and containing less than 0 1% free alkali In most soaps the free alkali, initially present as sodium hydroxide, is later more or less completely converted to sodium carbonate by absorp

[58] J Janota and H H Hull, *Oil & Soap* **17**, 96–100 (1940)

tion of carbon dioxide from the air during the drying operation The settled soap resulting from full boiling consists substantially of about 67–68% of actual soap, combined with about 32–33% of water It will contain a negligible amount of salt, and not more than about 0 5% glycerol Since there is some segregation and removal of metallic soaps and other impurities in the niger phase in the boiling operation, soap made by the full boiled process is lighter in color and purer than soap made from the same fat by other processes

Potash soap cannot be salted out easily and separated from the glycerol produced by saponification as can sodium soaps, since the addition of sodium chloride to a potassium soap leads to a double decomposition with the formation of sodium soap and potassium chloride Consequently, it is customary to prepare soft or potash soaps by the semiboiled process, in which the fat and alkali solution are simply weighed out in equivalent proportions and heated and mixed until saponification is effected There is some production of sodium soap by this method, but it is not generally favored because it makes glycerol recovery impossible and also because of the generally inferior quality of the soap produced It is difficult to adjust the proportions of alkali and fat so that there will be no substantial excess of either, or to obtain complete saponification of the fat even if the proportions are properly adjusted Whereas the free alkali content of a good full boiled soap will invariably be less than 0 1%, a semiboiled soap is generally considered satisfactory if it contains not over 0 3% free alkali The possible presence of unsaponified fat and the lack of any separation of impurities in the niger makes soaps of this type relatively susceptible to oxidation, with attendant discoloration and development of rancid odors Sodium hyposulfite or other antioxidant is usually added to minimize this susceptibility Semiboiled soaps of course retain all of the glycerol produced in the saponification process

In the manufacture of soap by the cold process the fat and the alkali solution are mixed to form an emulsion at a relatively low temperature, and the emulsion is then run into frames, where the saponification is completed The characteristics of cold made soaps are similar to those of semiboiled soaps

There is some production of soaps from fatty acids derived from the splitting of fats and oils Much of this soap is derived from acidulated foots or other low grade materials In chemical composition soaps of this class are not substantially different from ordinary full boiled soaps derived from a corresponding grade of fats, except that they contain no glycerol However, their physical properties may be different, soaps made from fatty acids are said to be softer than soaps made by the direct saponification of fats, and to be distinctive in texture It appears possible that the saponification of free fatty acids and the saponification of fats produce *different* microstructures in the finished soaps

(e) Milled Toilet Soaps

Toilet soaps of the more expensive grades are invariably of the milled type and are usually made from a full boiled soap base Milled soaps, which are produced from dried soap chips, worked and pressed into a coherent mass, are different in several respects from framed soaps, which are made by simply allowing the molten soap from the kettle to solidify in a large mass, which is later cut up into bars

Framed and milled soaps differ considerably in moisture content Although soap cakes of the framed type are dried to some extent in order to render them suitable for pressing this drying occurs only upon the surface and does not reduce the moisture content of the soap greatly below the approximate 33% of the neat soap as it comes from the kettle By drying the soap base in the form of very thin ribbons its moisture content may be readily reduced to 12% to 15%, which is that of most milled soaps A further important difference between framed and milled soaps is in the crystal modification of the soap crystals in the two products Framed soaps consist predominantly of soap in the omega phase, whereas in milled soaps the beta phase predominates (see the preceding discussion of the physicochemical nature of soaps, pages 328–338)

Since milled soap is less highly hydrated than soap solidified in the frame, it might be expected that it would be correspondingly more difficult to dissolve in washing operations Such, however, is not the case, due to the readiness with which soap in the beta phase is penetrated by water The penetration of water produces a layer of material upon the surface of the bar which, if not actually dissolved, is sufficiently softened to be readily removed and dispersed by mechanical action The tendency of a cake of soap to absorb water at the surface is not desirable to an unlimited extent If excessive, it produces a bar that is unpleasant to handle and wasteful to use However, it does have the apparent effect of improving the solubility and lathering properties of the soap

Since perfuming and coloring materials are incorporated into milled soaps while the latter are relatively cold, bars of this type may be much more readily perfumed than framed soaps Milled bars may also be produced with a bright, polished, surface finish impossible to obtain by any other means of processing

Milled soaps usually contain in the neighborhood of 20% of coconut oil or other oil of the lauric acid group In the highest grade of white soaps the remainder of the oil usually consists of a light colored tallow, and in some cases, hydrogenated whale oil In lower grades of white soap, or in colored soaps palm oil or hydrogenated fish oils may partially or wholly replace the tallow If the soap is to be colored, the soapmaker has a much wider variety of fats at his disposal than if it is to be white, since the colors added to the soap will mask the natural tints of highly colored or low grade oils

Good milled soaps do not contain more than 15% of water They do not contain rosin, or any filling or building material other than perhaps a fractional percentage of titanium dioxide or other white pigment, and in addition to water consist substantially of pure soap Their free alkali content should be less than 0 1%, calculated as NaOH The glycerol content of such soaps is not generally greater than about 0 75%

(f) Unmilled Toilet Soaps

Although most of the bar toilet soap made in the United States is a milled product made from a full boiled base, there is some manufacture of frame solidified toilet soap, saponified by the cold or semiboiled processes A good deal of this soap is made by small manufacturers, who favor these processes because they do not require expensive equipment or the services of an experienced soap boiler However, most of the large soapmakers customarily manufacture a few types of unmilled toilet soap

One of these types is Castile soap, which may be made wholly or largely from olive oil Other toilet soaps which are customarily unmilled are usually made from coconut oil They are popular in sections where the water is extremely hard, and for use with sea water, because of their ready lathering properties For use with soft water they are less desirable than soaps made from a blend of coconut oil with other fats They are considered rather harsh in their action on the skin, partly because some of them are high in free alkali content (often as high as 0 5%) and partly because of their high content of C_{10} and C_{12} soaps, to which many people are sensitive

Unmilled cold made toilet soaps are quite variable in their moisture content, which may vary between about 25% and 45% As noted above, they are often high in free alkali and usually contain in the order of 0 5–2 0% salt, sodium thiosulfate, sodium hyposulfite, etc , added as a preservative They also contain varying percentages of glycerol The cheaper grades are sometimes filled with sodium silicate or other alkalies

Unmilled toilet soaps, and particularly those made by the cold process cannot be as delicately perfumed as milled soaps, because of the fact that the perfuming materials must be added to the soap base while the latter is hot In the case of cold made soaps, any perfumes or colors used must be resistant to both heat and strong alkali Unmilled soaps are therefore less well perfumed and less commonly colored than milled soaps

(g) Special Bar Toilet Soaps

There are a number of more or less well defined types of special toilet soap bars which may be distinguished from the standard bar soaps mentioned previously

The so called *transparent or glycerine soaps* depend for their distinctive appearance upon the fact that soap is deposited from alcoholic solution in a

translucent, ultramicrocrystalline form[59] Glycerol and sugars also tend to cause soap to assume this form The effect is entirely physical, and depends upon the conditions under which the soap crystallizes rather than the presence of alcohol or any other substance in the finished soap cake Thus a transparent soap made with the aid of alcohol retains its appearance after most of the alcohol has been evaporated from it

Transparent soaps vary greatly in composition They may be prepared simply by dissolving soap flakes in alcohol and then driving off the greater part of the alcohol Such a product will not be greatly different in composition from the original soap flakes A more usual method of manufacture, however, is to add alcohol and glycerol, in the proportion of about two parts of alcohol to one of glycerol, to a hot saponified batch of semiboiled soap until a rapidly cooled sample is clear, after which the batch is framed in the usual way Sugar may also be added The fats used in transparent soaps usually are tallow and coconut oil Up to about 30% castor oil is often used in the fat charge, as the presence of this oil reduces the amount of alcohol, glycerol or sugar required to render the soap transparent The anhydrous soap content of transparent soaps is usually well under 50%

Castile soap is made either from pure olive oil or a mixture of oils which in most cases approximate the fatty acid composition of olive oil, usually by the cold process It is reputed to be less irritating to the skin than ordinary toilet soaps, and hence is in some demand as a medicinal soap and as a soap for infants, etc

The mildness of Castile soap, in comparison with ordinary toilet soaps of good quality, is due to the fact that it contains none of the medium molecular weight fatty acids which are present in coconut or palm kernel oils and which are somewhat irritating to the average skin The worst offenders in the way of skin irritation are said to be the soaps of capric and lauric acids, different individuals differ markedly in their reaction to these soaps By employing an oil consisting largely of oleic acid in the manufacture of Castile soap it is possible to obtain quite good solubility in the product without the benefit of coconut oil At the same time, the absence of a large proportion of linoleic or linolenic acid in the soap insures a fair stability toward oxidation

There is very little *mottled soap* consumed in the United States, but there is some demand for this product in certain other countries The blue streaks in a mottled soap, which are interspersed with a natural white or cream color, are due to the presence of a small amount (*ca* 0 25%) of ultramarine blue added to the soap kettle before the soap is finished By suitably finishing the soap in the presence of an excess of alkali, without separation of the niger, it may be charged to the frames in the form of two

[59] J W McBain and S Ross, *Oil & Soap*, 21, 97–98 (1944)

distinct but intermingled phases, one only of which contains the blue coloring material The final appearance of the finished soap is developed by very slow cooling in the frames Since the manufacture of a mottled soap in this fashion requires very careful control of the boiling process, mottled soaps are also prepared in some cases by careful hand mixing of a colored and an uncolored base

Mottled soaps do not usually contain more than about 50% of anhydrous soap, and are high in free alkali They are not usually made from fats of the highest grades and are often heavily filled with sodium silicate

Superfatted soaps are produced in limited quantity for use by people with very dry skins or others who wish a soap containing an excess of fat rather than alkali Superfatted soaps are less irritating than ordinary soaps to a very sensitive skin The superfatting agent, which is usually added to the amount of about 1%, is usually lanolin, but may be olive oil, peanut oil, or any other oil or fat Soaps of this type are prepared by incorporating the added fat in full boiled soap before the latter is milled Another special type of soap is made with an excess of alkali, consisting usually of about 5% of soda ash, for use where there is excessive oiliness of the skin

Carbolic or *carbolated* soaps do not usually contain carbolic acid or phenol but are made rather with the addition of a small percentage of commercial cresylic or tar acids Although the original appeal of such soaps was through their possible disinfectant value, it is dubious whether this value is very high in the case of most products, and generally the phenolic constituents serve merely to impart a distinctive odor to an ordinary milled toilet soap Carbolic soaps in the bar form are invariably colored, usually with a red dye This type of soap is also manufactured in liquid form

Pine tar soaps contain in the neighborhood of 5% of a special pine wood tar distillate which gives them a distinctive odor Considerable amounts of this type of soap are sold in bar form, although its greatest popularity is as an ingredient for a liquid shampoo Pine tar soaps have a distinctive black color

Mechanic's hand soap is marketed in a bar form, although somewhat greater quantities of this item are consumed in the form of powders and pastes This soap contains a large proportion, usually over 50% of pumice or other abrasive material, which is effective in removing deeply imbedded dirt or grease from the hands Since it is low in its content of anhydrous soap, such soap as it does contain must lather freely, in order to make its over all lathering properties comparable to those of an ordinary toilet soap The base for a mechanic's hand soap is often a cold made coconut oil soap filled with sodium silicate

A great variety of *medicated soap* bars have appeared on the market from time to time They usually consist of a milled product in which the me

dicament is worked into the soap in the milling operation The agents which have been used in medicated soaps include mercuric iodide, sulfur, insecticides of the pyrethrum type (for animals), iodine, ichthyol, etc

(h) Shaving Soaps and Creams

In shaving soaps, as in other toilet soaps, detergency is important The shaving soap must remove the oily coating normally present on the beard so that the latter may become softened through the absorption of water However, the lather produced by the soap also provides the absorbed water, so the lathering qualities are equally important A good shaving soap or cream must dissolve readily, form a heavy, fine grained and abundant lather which will not break down or dry out during the shaving operation, and be free of any tendency to irritate the tender surfaces of the newly shaved face

Shaving bars and sticks are usually made by the semiboiled or cold processes since a certain proportion of glycerol in the finished product is desirable, to prevent drying and for its effect on the quality of the lather It is essential that shaving soaps contain no free alkali, either in the form of hydrate or carbonate This is usually assured by superfatting the soap with 0 5% to 1 0% of stearic acid

Since it is stearic acid soaps that produce the close, thick lather desirable in a shaving soap, there must be a high percentage of this constituent in the fatty materials used Usually not less than one third of the total fats consist of commercial stearic acid Coconut or palm kernel oil is also a customary ingredient to the amount of 20% to 35% of the total fats The remaining fat may be tallow, palm oil, olive oil, etc

A sodium soap made to the approximate formula indicated above would be entirely too hard and insoluble, therefore it is necessary to conduct the saponification partly with caustic potash instead of caustic soda The percentage of potash soap in the finished product will vary somewhat with the ratio of stearic acid to unsaturated or shorter chain saturated acids in the fat charge but will not usually be less than half that of the sodium soap

The production of shaving soap is much exceeded by that of shaving cream, which is packaged in collapsible tubes Shaving creams vary somewhat in composition Some consist merely of the potassium soaps of a mixture of relatively soft oils However, in the type of shaving cream which is most popular in the United States, the ingredients are essentially the same as those of shaving soap, with suitable changes in the proportions, to maintain the cream in a soft, plastic form, easily pressed from the tube and distributed on the bristles of the shaving brush and on the face

In this type of shaving cream somewhat greater proportions of stearic acid are used than in shaving soaps, and correspondingly lesser amounts of

coconut oil and tallow or similar fats More caustic potash and less caustic soda is used and also more water The product is also more heavily super fatted Shaving creams usually contain about 35% anhydrous soap in the proportions of about 1 part sodium soap to 5 parts potassium soap They contain in the neighborhood of 5% free fatty acids, which are usually gen erated in the soap by the addition of the proper amount of sulfuric, hydro chloric or boric acids The presence of a large percentage of free stearic acid in the cream is responsible for its distinctive sheen, and also is said to contribute in an important way to the soft body of the product

The latherless or "brushless" shaving creams, which have recently become popular, are essentially oil in water emulsions similar to vanishing creams The oil in these creams is usually mineral oil, although a vegetable oil may be used Surface active materials are incorporated, to stabilize the emulsion and to assist in wetting the beard so that it will readily ab sorb water A considerable variety of surface active agents are used in the different preparations In one type of cream the aqueous phase consists of a paste of superfatted potassium soap largely made from stearic acid In another type the potassium stearate is replaced with triethanolamine soaps Still others employ sulfonated tallow or other sulfonated oils All types contain the maximum amount of water consistent with the proper body in the product, i e, about 70% to 80%

(i) *Powdered Soaps*

Powdered soaps are used in considerable quantities in dentifrices and miscellaneous toilet preparations Most powdered soap is a tallow-coconut oil product, saponified by the full boiled process and then flaked, dried to a near anhydrous condition, and ground Such soap is not made by the cold or semiboiled processes because the presence of glycerol makes the grinding difficult Soaps made by these processes are also less stable than full boiled soaps Stability is highly important in this product, because of the surface exposed to oxidation

Powdered soap intended for use in dentifrices is usually made of the very highest grade materials, in order to minimize taste or odor Since the soaps of the low molecular weight fatty acids of coconut oil have a slight soapy taste, a full boiled soap of the Castile type is preferred by some users al though it is less stable toward oxidation than soap containing coconut oil

(j) *Shampoos*

Liquid shampoos are used in large quantities in the home and in barber and beauty shops for washing the hair The principal requirements in a shampoo are an ability to produce a profuse but light lather and to rinse readily from the hair These requirements are best met by a soap contain

ing a large proportion of coconut oil Many liquid shampoos are simply solutions of potash coconut oil soap, although some contain a minor proportion of soap derived from olive oil or other soft oil Coconut oil soap also has the advantage of being very soluble and hence unlikely to jell in the bottle at low temperatures

The usual percentage of real soap in a liquid shampoo is about 20–25% When a shampoo is made up to this strength it will usually show some tendency to cloud at low temperatures, because of the separation of small amounts of stearic and other fatty acid soaps of high molecular weight As the trade demands an absolutely clear, sparkling product, it is necessary to employ a winterizing treatment, in which the solution is chilled and held at a low temperature for a somewhat prolonged period before it is filtered and bottled

Since any variety of soap tends to deposit insoluble calcium and magnesium salts from ordinary waters, and since these are very detrimental to the appearance of the hair, nonsoap detergents are quite widely used in shampoos The materials formerly used for this purpose consisted chiefly of sulfonated olive and castor oils, but these have now largely been supplanted by salts of sulfated fatty alcohols The most popular preparation of this kind is substantially a solution of an amine salt of lauryl sulfate

(k) *Bar Laundry Soaps*

The materials known as laundry soaps are not used in commercial laundries, but are employed in the household for laundry, dishwashing and general cleaning Household soaps in bar form are not as popular now as they were formerly, due to the introduction of many brands of packaged flakes, granules, beads, etc , but are still produced and consumed in very large quantities

The two principal varieties of laundry soap are white and yellow *White laundry soap* is usually a full boiled product made from 25–40% coconut oil and 60–75% tallow, hydrogenated fish oil, etc It is always prepared with sodium silicate or other soap builder, in sufficient amount to reduce its anhydrous soap content to somewhat less than 50% and is never milled

Yellow laundry soap is similar to white laundry soap except that it contains a substantial proportion of rosin The rosin imparts to the bar a distinctive yellow color Rosin soap is relatively soft and sticky, hence yellow soaps cannot be prepared with as much builder as white soaps Their anhydrous soap content is usually over 50% It is also usual to employ less coconut oil in yellow than in white laundry soap, because of the relatively high solubility of rosin soap

Naphtha soap usually consists of a white laundry soap, to which has been added a small percentage of petroleum naphtha The naphtha volatilizes

from the soap quite readily, hence the amount in the finished bar, as it is delivered to the consumer, is quite variable In the United States a soap cannot legally be sold as a "naphtha soap" unless it contains at least 1% of the hydrocarbon In a concentration approaching the lower legal limit the naphtha is of doubtful value in reinforcing the detergent action of the soap

Marine or salt water soaps are principally used for laundry purposes on board ships They must have special characteristics which enable them to lather and clean effectively in sea water

The marine soaps produced in the past have invariably consisted of cold made or semiboiled products made from coconut or palm kernel oils, usually with the addition of sodium silicate as a builder In the absence of an adequate supply of coconut or other lauric acid oils the United States Navy has recently issued new specifications for a marine soap consisting of a tallow soap to which is added a minimum of 20% of a synthetic detergent It is provided that the synthetic detergent shall preferably be of the general formula, A R SO_3Na, in which A is an alkyl radical containing 10 or more carbon atoms and R is an aromatic or aliphatic grouping Soaps made to this formula are said to be generally superior to the older coconut oil soaps

(l) *Floating Soaps*

Floating soaps comprise the one variety of soap that is extensively used for both toilet and laundry purposes They are generally made with coco nut oil and a hard white fat such as tallow or hardened marine oil, without the use of builders, hence are not greatly different in composition from or dinary milled toilet soaps Their ability to float arises from their high content of incorporated air This air, like that in shortening, is dispersed in the form of very small bubbles, and is invisible to ordinary inspection

They are particularly esteemed as a bath soap, and are also much used in place of the cheaper white laundry soaps for dishwashing and general household purposes They are less irritating to the hands than ordinary laundry soaps, since they consist of pure soap with no alkaline builder In appearance they more closely resemble laundry soaps than toilet soaps, as they are molded in large white bars and are not highly perfumed

Formerly, floating soaps were made by simply preparing a full boiled base and crutching into this the desired amount of air, after which the soap was framed, slabbed, cut and stamped in the usual way Lately, however, the larger manufacturers of this product have adopted continuous methods of aerating and solidifying the product in specially designed equipment The soaps produced by these methods are principally in the beta form and hence somewhat resemble milled soap in the ease with which they form a hydrated surface layer

(m) *Soap Flakes, Granules, and Beads*

In late years soap flakes, granules, and other quick dissolving forms of soap have to a considerable extent replaced bar laundry soap for dishwashing, laundry work, and general household cleaning (see Table 117, page 327)

The quick-dissolving soaps are divided into two distinct classes, namely those consisting of pure soap, and those to which an alkaline builder has been added The former are a relatively high priced product and find their chief use in dishwashing and the home laundering of silks, woolens, and other fine articles of clothing The products which contain builders are primarily general purpose home laundry soaps

Soap chips or flakes are produced by chilling the molten soap in a thin sheet and then drying and breaking or cutting up the solidified sheet Beads and granules are produced by spray drying Beads are distinguished from granules by having the form of hollow rather than solid spheres Thus their apparent density is very low Both pure soap and builded soap are produced in all the various quick dissolving forms, with one important exception the so called polished flakes, which are given a special milling treatment to improve their smoothness and luster, are invariably a pure soap product These flakes are among the most expensive of the packaged soaps They are invariably white, and are made from a base containing a considerable percentage of coconut or other lauric acid oil in combination with well bleached tallow or other hard, light colored fat Thus they are not different in composition from the high grade floating soaps except in moisture content, and may in fact be considered the quick dissolving counterpart of the latter

The flakes, chips, granules etc, which are packaged for household use may be made from a variety of fats, but they usually contain coconut oil or similar oil when such oil is available for the sake of the solubility and quick lathering properties which it confers High solubility and quick suds formation are particularly important in the pure soap products, since these are much used in cold or lukewarm water In addition to the flakes and chips sold in household packages there is a large consumption of bulk chips, chiefly by commercial laundries Bulk chips usually consist of pure tallow soap

The quick-dissolving soaps contain much less moisture than bar soaps, since with a high water content they tend to cake in the package Pure soap flakes, in particular, are extremely low in moisture, containing usually less than 5% Granules and beads may contain 10% to 15% water The percentage of builder incorporated in quick-dissolving builded soaps is quite variable, but is usually not less than about 15% Formerly, the builders employed were principally soda ash and sodium silicate Re

cently, however, there has been a strong trend toward the use of the more efficient tetrasodium pyrophosphate

(n) *Washing Powders*

Washing powders are relatively cheap detergents consisting of a small proportion of soap mixed with a large proportion of soda ash or other alkaline material The amount of real soap in these powders is quite variable, but is in general much less than 50% and often not greater than 10% to 20% Although the standard alkaline ingredient for washing powders is soda ash, trisodium phosphate, or other builders are sometimes used

Washing powders are principally made by pulverizing the mixed and dried product in various types of mills, although recently there has been a tendency to adopt the method of spray drying for washing powders

The consumption of this material is about equally divided between household and bulk users The use of washing powders in the household appears to have somewhat declined recently, this is probably due to the increased popularity of builded granulated soaps

(o) *Scouring Soaps and Cleansers*

Scouring soap cakes are compounded from a finely ground siliceous material with only sufficient soap and soap builder to hold the cake together The usual proportions are about 80% abrasive and approximately 10% each of soda ash or other alkaline builder and soap The soap usually contains a sufficient amount of coconut oil to produce an appreciable lather These soaps are chiefly used for cleaning and polishing windows, display cases and similar smooth, highly polished surfaces

The cake form of scouring soap is much less popular than powdered scouring soaps or cleansers, which are widely distributed, both in household packages and in bulk Cleansers are more or less similar in composition to cake scouring soaps, except that they contain less soap and the soap is usually made from lower grade fats A popular brand contains 2% anhydrous soap, 4% soda ash, 7 5% trisodium phosphate, and about 78% silica The remainder consists of combined water Cleansers are much used in the household for cleaning kitchen utensils, bath tubs, sinks, etc

(p) *Liquid Soaps*

Liquid toilet soaps find their principal use in public wash rooms, since they are easily dispensed from automatic or semiautomatic devices They consist of aqueous solutions of soap made from potash and coconut oil or other lauric acid oil, mixed with a soft oil such as cottonseed, soybean, or peanut oil The concentrated base is usually diluted for use to a soap content of about 15% Liquid toilet soaps are not essentially very different from liquid shampoos, except that they are commonly made from lower

grade oils, are not perfumed and are not as carefully clarified The principal object in preparing a liquid toilet soap is to produce a solution which will not clog the dispenser, and which will form a satisfactory lather in the amount customarily discharged into the hand

Liquid floor soaps are made in considerable quantities for washing linoleum, tile, and composition floors in offices, schools, institutions, and various public buildings These soaps usually contain about 25% anhydrous soap, which is usually a superfatted soap of linseed or soybean oil They are often compounded with a small percentage of pine oil In the washing of floors it is particularly necessary that no alkaline residue be left after the floor is washed and rinsed Such a residue is unsightly and is also injurious to paint or linoleum surfaces By using a superfatted soap it can be assured that any residue will be oily rather than alkaline If the residue consists of a drying oil it will oxidize to produce a nonoily protective coating

(q) *Miscellaneous Industrial Soaps*

A special class of soaps is manufactured for use in the organic solvents employed in dry cleaning operations Dry cleaners' soaps are usually potash products containing an excess of 5-10% of free fatty acids, most of which consists of oleic acid In other dry cleaners' soaps, triethanol amine is used instead of caustic potash as the saponifying alkali Obviously no large percentage of water can be tolerated in this class of soaps, hence saponification is carried out in the medium of an organic solvent, and the soap is marketed in the form of a solvent-soap paste or liquid containing 10-15% actual soap

Automobile soaps are usually superfatted potash soaps made from linseed, corn, or soybean oils Except for the fact that they are usually sold in paste rather than liquid form, they are similar to linoleum floor soaps

A number of special soaps are made for scouring and cleaning operations in the manufacture of textiles Although requirements for textile soaps are not exacting insofar as color, odor, etc , are concerned, and these soaps are usually made with cheap fats, some care is nevertheless required in their manufacture In general, textile soaps must be free from builders and must be soluble at reasonably low temperatures, since textile fibers, particularly silk and wool, are injured by contact with alkalies at high temperatures Relatively little tallow or coconut oil is used in making textile soaps, the principal fats used for the purpose are olive oil or olive oil foots, palm oil, corn, cottonseed, and peanut oil foots, distilled fatty acids, and greases Most of the textile soaps are sodium soaps The cold, semiboiled, and full-boiled processes are all employed in their manufacture

Insecticide soaps are almost invariably made from caustic potash and

one of the fish oils Wire-drawing soaps consist of ordinary tallow or grease soaps containing added talc The soap employed as an emulsifying agent in the polymerization of butadiene to make synthetic rubber is a pure tallow chip product

5. Surface-Active Agents Other Than Soap

Since the hydrophilic portion of a surface-active compound may consist of any one or a combination of the following groups.[3] —OSO_2ONa, —COONa, —SO_2ONa, —OSO_2OH, —SO_2OH, —OH, —SH, —O—, =CO, —CHO, —NO_2, —NH_2, —NHR, —NR_2, —CN, —CNS, —COOH, —COOR, —OPO_3H_2, —OPO_2H_2, —OS_2O_2H, —Cl, —Br, —I, —$CONH_2$, —CONHR, —$CONR_2$ and the lipophilic portion may be any fairly long chain (usually aliphatic, but sometimes mixed aliphatic–aromatic), with or without unsaturated linkages or substituted groups, it is obvious that the possible variety in surface active agents is almost limitless

A recently compiled list[60] of commercially available surface-active agents includes 243 different members This list contains many duplications, of identical compounds sold under different trade names, but on the other hand it omits many industrially important materials, including most of those used in food preparations

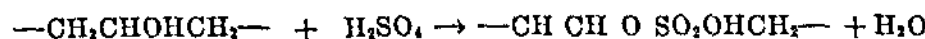
It is impossible in a publication of this nature to give consideration to all of the surface active agents of potential or even actual commercial importance Reference will be made, therefore, only to a few of the more important types

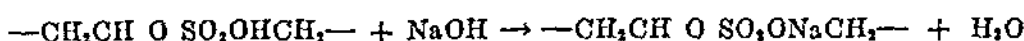
(a) *Sulfated Oils*

Sulfated oils are the oldest of the nonsoap surface active agents, having been used in the textile industry for over a century These oils are commonly termed "sulfonated oils," but technically speaking the term is a misnomer The compounds chiefly resulting from "sulfonation" are sulfates, as represented by the grouping, —CH_2 O SO_2OH Sulfonates, which contain a direct carbon-to-sulfur linkage, —CH_2 SO_2OH, are produced in only very minor amounts In discussing surface-active agents it is necessary to make a distinction between the two classes of compounds, since in many cases the properties of sulfates and the corresponding sulfonates are quite different

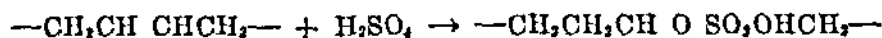
Oils are sulfated by treatment at a low temperature with strong sulfuric acid, with subsequent washing and neutralization of the sulfated mass In castor oil sulfation appears to take place chiefly at the hydroxyl group of ricinoleic acid:

[60] F J Van Antwerpen, *Ind Eng Chem*, 35, 126–130 (1943).


$—CH_2CHOHCH_2— + H_2SO_4 \rightarrow —CH\ CH\ O\ SO_2OHCH_2— + H_2O$


$—CH_2CH\ O\ SO_2OHCH_2— + NaOH \rightarrow —CH_2CH\ O\ SO_2ONaCH_2— + H_2O$

In ordinary fats and oils sulfation occurs at the double bonds of the fatty acids

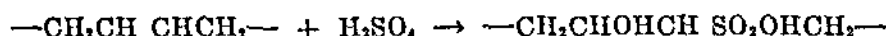

$—CH_2CH\ CHCH_2— + H_2SO_4 \rightarrow —CH_2CH_2CH\ O\ SO_2OHCH_2—$


$—CH_2CH_2CH\ O\ SO_2OHCH_2— + NaOH \rightarrow$


$—CH_2CH_2CH\ O\ SO_2ONaCH_2— + H_2O$

The fatty acids of the oil are sulfated more or less preferentially, according to their degree of unsaturation

There are a number of side reactions so that commercial sulfated oils consist of a complex mixture containing many substances other than sulfated glycerides and other glycerides which may have escaped sulfation There is in particular a large production of free fatty acids, from hydrolysis of the glycerides, some of the free acids are of course also sulfated This hydrolysis is accompanied by partial conversion of the neutral oil to mono and diglycerides There is a minor production of sulfonic acids


$—CH_2CH\ CHCH_2— + H_2SO_4 \rightarrow —CH_2CHOHCH\ SO_2OHCH_2—$

In the sulfation process itself and also during washing and neutralization there is some degree of hydrolysis of the fatty acid sulfates, to form hydroxy acids

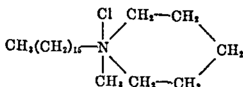

$—CH_2CH\ O\ SO_2OHCH_2— + H_2O \rightarrow —CH_2CHOHCH_2— + H_2SO_4$

The hydroxy acids are quite reactive under the conditions of sulfation and may undergo condensations to form lactones, lactides, and estolides [61] Estolides are probably also formed by the direct reaction of fatty acids and fatty acid sulfates In some oils, particularly highly unsaturated fish oils there is oxidation of the unsaturated fatty acids, accompanied by polymerization of the products of oxidation Iso oleic acid has been found in sulfonated oils,[6] and it is probable that there is other fatty acid isomerization during the reaction

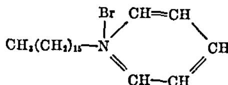
Since sulfation occurs more readily at the hydroxyl group of ricinoleic acid than at the double bonds of unsaturated fatty acids, the sulfation of castor oil (to produce the Turkey red oil of commerce) proceeds with less extensive side reactions than does that of other oils The complete characterization of sulfated oils is naturally a matter of extreme difficulty, but it is possible to separate samples roughly into neutral or unreacted oil, unreacted fatty acids, and sulfated material, by proper procedures, and to

[61] D Burton and G F Robertshaw *Sulphated Oils and Allied Products* Chemical Pub Co New York 1942

[62] R M Koppenhoefer, *J Am Leather Chem Assoc*, **34**, 622–639 (1939)



Cetyl methyl piperidinium chloride



Cetyl pyridinium bromide

A more or less related group of surface active compounds are the amine salts of high molecular weight, represented typically by dodecylamine hydrochloride



$$CH_3(CH_2)_{10}CH_2\ NH_2\ HCl$$

An important point of difference between this class of surface active agents and others is that these are cation active, i e they form solutions in which the ion comprising the larger part of the molecule is positively charged Thus they have the same stability in acid solution that soap and other anion active agents have in alkaline solution Since the large ions are positively charged, they of course cannot react with the calcium and magnesium ions present in natural waters

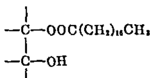
The principal use of cation active agents is in the processing of cotton textiles Used as assistants in the dyeing of cotton materials, their function is to inhibit wetting They retard the adsorption of dyes by cellulosic materials and thus promote even or level dyeing [65] They also restrain the bleeding of water soluble dyes in detergent operations subsequent to dyeing

(f) *Partial Esters of Polyhydric Alcohols*

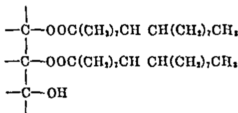
If a polyhydric alcohol is but partially esterified with fatty acids, the resulting compound will possess surface activity due to its combination of aliphatic chains with free hydroxyl groups The alcohols which may be so esterified include glycol, glycerol, polyglycols, polyglycerols, sorbitol, pentaerythritol, etc

The solubility of these compounds depends upon the balance existing between their lipophilic and hydrophilic properties, which may vary greatly according to the relative numbers of fatty acid chains and hydroxyl groups and the positions of the groups Mono and diglycerides are oil soluble but water insoluble However, polyglycerols and polyglycols

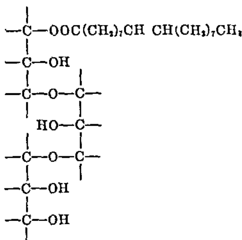
[65] J E Smith *Ind Eng Chem*, **31**, 40–43 (1939)



Glycol monostearate



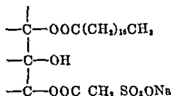
Glycerol diolein



Triglycerol monoolein

composed essentially of mono esters of high polymers may be water soluble and have detergent properties Detergent compositions containing these substances have been patented [66]

The partial esters of glycerol, sorbitol, polyglycerols, etc are edible and find their greatest use as emulsifying agents in food products A mixture of mono- and diglycerides is manufactured in large quantities for use in superglycerinated shortenings (see Chapter IX) A related compound, monostearin sodium sulfoacetate, is extensively used as an antispattering agent in margarine (see Chapter X)



Monostearin sodium sulfoacetate

(g) Chlorinated Aliphatic Esters

Chlorinated esters of fatty acids have proved valuable as surface active agents for lubricating oils [67-69] Added to a mineral oil in the amount of 1% or less, they form oriented layers which are strongly adsorbed at metal surfaces The formation of adsorbed layers insures a protective film be

[66] R Furness and A Fairbourne (to Lever Bros , Ltd), British Pats 439,435 (1935) and 442 950 (1936)

[67] G L Clark B H Lincoln and R R Sterrett, *Proc Am Petroleum Inst* , *III*, **16**, 68–80 (1935)

[68] L L Davis, B E Sibley, and B H Lincoln, *Proc Am Petroleum Inst* , *III*, **16**, 81–103 (1935), *Refiner & Natural Gasoline Mfr* , **14**, 523 536 (1935)

[69] B H Lincoln, G D Byrkit, and W L Steiner, *Ind Eng Chem* , **28**, 1191–1197 (1936)

CHAPTER XIII

PAINTS, VARNISHES, AND RELATED PRODUCTS

1. Introduction

Paints, varnishes, and other decorative and protective coatings,[1] including printing inks, comprise one of the three major fields of oil and fat utilization In 1941, the factory consumption of oils in paints and similar products in the United States amounted to 600,121,000 pounds While this amount of oil is considerably less than that consumed in soap in the same year (2,143,857,000 pounds), or in the manufacture of shortening, margarine and other edible products (2,247,658,000 pounds), it exceeds the oil used in any other single class of products

The drying oils owe their value as materials for protective coatings to their ability to polymerize or "dry" after they have been applied, to form tough, adherent, impervious, and abrasion-resistant films Their film-forming properties are closely related to their degree of unsaturation, since it is through the unsaturated centers or double bonds that polymerization takes place With the exceptions to be noted later, the oils used in paints, varnishes, and similar products are relatively high in iodine value In any given product, there is an optimum degree of reactiveness in the oil, the speed with which the oil dries must be balanced against such factors as elasticity and durability in the paint film In general, however, unsaturation may be said to be at a premium in paint and varnish oils, and the oils which are in the greatest demand are those in which oxidation and polymerization take place most readily

Until quite recently, the oils consumed in paints, varnishes, etc, consisted entirely or almost entirely of oils with pronounced drying properties, belonging to the linolenic and conjugated acid groups Lately, however, synthetic resins of strong polymerizing properties have become available for use in varnishes and enamels in place of natural resins With these materials it has become possible to make a considerable use of oils with poor drying, and in some cases, even nondrying properties In these

[1] GENERAL REFERENCES H K Dean, *Utilization of Fats*, Chem Pub Co, New York, 1938 C Ellis, *Printing Inks*, Reinhold, New York, 1940 N Heaton, *Outlines of Paint Technology*, 2nd ed, Lippincott, London, 1940 J J Mattiello editor, *Protective and Decorative Coatings*, Vol I, Wiley, New York, 1941, Vol III, 1943, Vol IV, 1944 Oil and Colour Chemists' Assoc, *Varnish Making*, Chemical Pub Co, New York, 1940

latter products, the function of the oil is more that of a plasticizer than an active drying ingredient Also, significant quantities of a strongly drying oil are now made artificially, by the dehydration process, from castor oil, which in its natural state is completely nondrying Additional processes have been developed to varying degrees of perfection for conferring drying ability upon other oils which are naturally deficient in this property None of these latter processes is of great commercial importance at the present time, but together they constitute a potential means of supplementing present sources of paint and varnish oils from materials which have heretofore been devoted to other uses

TABLE 123

FACTORY CONSUMPTION OF DIFFERENT OILS IN THE MANUFACTURE OF PAINTS AND OTHER FINISHES AND PRINTING INKS IN THE U S IN 1941[a]

Oil	Consumption thousand lbs	
	Paints etc	Printing inks
Cottonseed oil	196	153
Coconut oil	919	1
Corn oil	848	34
Soybean oil	41,594	255
Olive oil, inedible	4	—
Rapeseed oil	103	—
Linseed oil	373,745	23 547
Tung oil	48,825	2,960
Perilla oil	5,408	831
Castor oil	44,240	760
Palm oil	—	1
Other vegetable oils	13,690	89
Lard	—	13
Tallow, inedible	364	10
Grease	150	472
Neatsfoot oil	37	—
Marine mammal oils	26	10
Fish oils	40,653	179
TOTAL	570 802	29,319

[a] U S Bur Census, *Animal and Vegetable Oils*, 1938-1942 Washington, 1943

Modern requirements in protective coatings are extremely diverse and in many cases exacting They go far beyond the mere necessity of protecting the finished surface from the weather or from ordinary wear or abrasion Some coatings, as for example those employed as electrical insulation, must possess extreme resistance to high temperatures, or to penetration by moisture Others, such as marine varnishes, and enamels for the interior of tin cans, must withstand prolonged contact with water or aqueous solutions The exigencies of modern, assembly line methods of manufacture produce many particular requirements, and have created an especial demand for quick-drying finishes The wide distribution of illustrated journals and advertizing matter and the development of high-

speed printing processes have greatly elaborated the requirements of users of printing inks

The exacting requirements of modern industry have to a large extent removed the manufacture of paints and varnishes from the category of an art to that of a science In most plants the manufacturing processes are now carried out under careful laboratory control, and are freely modified or revised, whenever revision is indicated, in accordance with known scientific principles As a result, the industry has been able to offer a a succession of constantly improved products through a period marked by severe fluctuations in the availability of many important raw materials

In the past several years, there has been a pronounced trend away from the practice followed by some users of blending their own paints and var

TABLE 124
FACTORY PRODUCTION OF PAINTS VARNISHES AND SIMILAR PRODUCTS IN THE U S IN 1939[a]

Product	Amount manufactured	Value m ll on dollars
Paints, paste form	254,409 405 lbs	25 1
Paints, ready mixed and semipaste	107,859,374 gals	158 0
Varnishes, synthetic resin	23 826,438 gals	29 7
Varnishes natural resin	14,113,029 gals	14 0
Varnishes, spirit	7,787,560 gals	8 4
Varnishes other	12,653,264 gals	12 4
Varnish stains	2,236,103 gals	3 6
Enamels, synthetic resin	21,341,559 gals	42 9
Enamels natural resin	18,908,607 gals	33 1
Japans, drying	2,784,203 gals	2 3
Japans, baking	1,939,737 gals	1 5
Nitrocellulose products	—	64 3
Putty	103,232,417 lbs	3 8

[a] U S Bur Census *Census of Manufacturers*, Washington, 1939

nishes The finishes now on the market are for the most part formulated by the manufacturer for specific and often highly specialized uses, and are sold in a form suitable for immediate application Even house paints are now largely distributed in the ready mixed form (Table 124)

As mentioned previously, an important modern development has been the creation of a very large demand for varnishes, enamels and other fast drying finishes At present, the production of ordinary paint in the United States is probably exceeded in volume by that of the latter class of products (Table 124)

Many of the more important recent developments in the technology of paint and varnish oils have been concerned with means for supplying the demand for fast-drying finishes of high durability Since tung and other conjugated acid oils are particularly suitable for the manufacture of such products, the consumption of these oils has increased greatly in recent

years Imports of tung oil into the United States first became large in about 1910, when they amounted to 43,000,000 pounds In subsequent years, imports were more or less variable because of unsettled political conditions in China, but their trend was generally upward In 1937, imports reached a maximum of 173,000,000 pounds[2] However, the subsequent outbreak of war in the Far East had the effect of first limiting and eventually eliminating the exportation of Chinese oil

The disappearance of Chinese tung oil from the market led to a drastic shortage of natural conjugated acid oils, since the production of American tung oil and Brazilian oiticica oil is relatively small, even in the most favorable seasons, and in addition is extremely variable

The shortage of natural conjugated acid oils has greatly stimulated the production of an artificial conjugated oil made from castor oil by the dehydration process At the present time, most of the conjugated acid oil available consists of the dehydrated castor product Most of the 44,000,000 pounds of castor oil consumed by the paint and varnish industry in 1941 (Table 123) was dehydrated, and the consumption in more recent years has undoubtedly been even greater

Another important development in the paint and varnish industry has been the introduction of synthetic resins as replacements for natural resins in the manufacture of varnishes and enamels The synthetic resins which are used in protective coatings include those of the alkyd, maleic, phenol-formaldehyde, urea-formaldehyde, coumarone indene, acrylic and vinyl types Certain of these may be produced in an oil soluble form and combined with a drying oil to produce a varnish, in a manner similar to that employed in making similar products with fossil resins Others are incompatible with drying oils and are used only in coatings of the lacquer or spirit varnish type

By use of the synthetic resins it has been possible to produce a variety of coatings which in many cases have important points of superiority over any of those compounded from natural resins The synthetic varnishes and enamels are particularly distinguished by their hardness and durability and their high degree of resistance to the action of water, alkalies, and other chemical agents

The widespread use of synthetic resins has increased the relative demand for conjugated acid oils, inasmuch as these resins, particularly those of the phenol formaldehyde variety, are most successfully compounded with this type of oil

2 Mechanism of Oil Drying

When a paint, varnish, or other coating material consisting preponderantly of drying oils is applied to a surface, the following successive

[2] U S Bur Census, *Animal and Vegetable Oils*, 1938–1942 Washington, 1943

changes are observed to take place in the applied film· First, the oil in the film becomes increasingly thick and viscous, and finally tacky Secondly, the film solidifies, and then over a period of hours or days, becomes increasingly firm and tough The phenomenon bears a superficial resemblance to that occurring in many aqueous systems with the evaporation of water, hence has been termed "drying" Actually, of course, this term is a misnomer, the paint contains no water, and the essential part of the drying operation involves no evaporation in the proper sense of the term

The drying of a paint film ordinarily involves oxidation It proceeds very slowly at ordinary temperatures in a vacuum or in an inert gas It is accelerated by heat, by light, and by the presence of certain metallic salts or "dryers," such as the soaps of lead, cobalt or manganese If a batch of drying oil is subjected to a prolonged high temperature, with or without oxygen being present, a similar series of changes takes place, the oil thickens and eventually solidifies in the form of a gel This property of drying oils is taken advantage of in the manufacture of quick-drying paints and varnishes If the drying oil is partially thickened by heat before it is mixed into the paint, the drying time of the latter is accordingly shortened

Dried paint films possess the elasticity, cohesiveness and homogeneity which are characteristic of the typical gel structure They are infusible and to a considerable extent insoluble in ether, acetone, and other oil solvents Obviously, they represent a state of molecular aggregation very different from that in the undried oil

The drying of oils has been observed through many centuries, and the mechanism of drying has long been under investigation by chemists and physicists These investigations have by no means been fruitless, they have, on the contrary, revealed much information of both practical and theoretical value A complete and generally accepted theory of oil bodying and drying has yet to be advanced, however, and many fundamental considerations are still subjects of controversy

Recent reviews on the subject of oil drying, which include more or less comprehensive but divergent theories of the process are those of Morrell,[3] Bradley,[4] Von Mikusch and Priest,[5] Rudd,[6] and Hollis [7]

(a) *Comparison of Heat Bodying and Ordinary Film Formation*

The processes of heat bodying and natural drying in paint and varnish oils are apparently similar in a number of respects In both cases the oil

[3] R S Morrell, *Chemistry & Industry*, **56**, 795–798 (1937)
[4] T F Bradley, *Ind Eng Chem*, **29**, 440–445 (1937)
[5] J P Von Mikusch and G W Priest, *Oil & Soap*, **18**, 50–59 (1941)
[6] H W Rudd, *Paint Manuf*, **13**, 95–103 (1943)
[7] C E Hollis, *J Oil Colour Chem Assoc*, **27**, 67–91 (1944)

undergoes an irreversible change from a liquid to a gel The oils which dry most rapidly undergo thickening and gelation most readily under the influence of heat Both reactions are accelerated by the presence of metallic "dryers" and are inhibited by antioxidant substances Furthermore, in the case of synthetically prepared esters of various alcohols and fatty acids, the compounds which readily form gels under the influence of heat are likewise the ones which form hard paint films

The greater part of the laboratory investigations on drying oils to date have been concerned with the operation of heat bodying rather than ordinary film drying, which is a somewhat more difficult subject for study The two reactions differ in one important particular Atmospheric oxidation is an element of predominant importance in ordinary drying, whereas oils may form gels when heated *in vacuo* or in an inert gas Thus molecular aggregation in the case of air drying is conceived to be the result of interaction between reactive peroxides or other oxygenated substituents formed by the union of oil and oxygen In the case of heat bodying, there appears to be a direct carbon to carbon union of fatty acid radicals, without the intervention of oxygen However, regardless of the differences in the chemical reactions in the two cases, it appears likely that the fundamental mechanism of molecular growth or polymer formation is essentially similar in the two cases

The two different modes of molecular combination, polymerization through oxidation and polymerization through the influence of heat, are respectively exemplified in commercial paints and varnishes Although the use of heat bodied oils in paints is not uncommon, the drying of coatings of this class is largely the result of atmospheric oxidation, in the applied film In the manufacture of varnishes, the process of polymerization is carried to an advanced state in the varnish kettle, often with the aid of an added resin of reactive properties The cooked varnish is then mixed with a volatile "thinner," in order to reduce it to a consistency suitable for application and a large part of the drying of the applied finish consists simply of the evaporation of the thinning solvent Oxidation plays a relatively minor rôle in the formation of the dried film.

(b) *Extent of Molecular Aggregation in Bodying and Drying*

Since some species of molecular aggregation is obviously involved in the thickening and subsequent gelation of oils, a number of investigators[8-13]

[8] B P Caldwell and J Mattiello, *Ind Eng Chem* 24, 158–162 (1932)
[9] E Elod and U Mach, *Kolloid Z* 75, 338–348 (1936)
[10] J S Long and W J Arner, *Ind Eng Chem* 18, 1252 1253 (1926)
[11] J S Long and J G Smull, *Ind Eng Chem* 17, 138–141 (1925)
[12] J S Long and G Wentz, *Ind Eng Chem* 17, 905–908 (1925)
[13] J S Long and G Wentz, *Ind Eng Chem* , 18, 1245–1248 (1926)

have attempted to determine the average molecular weights of the thickened or gelled oils and their soluble and insoluble fractions in different solvents Unfortunately, such determinations are beset with considerable difficulty It is impossible to examine the portions of oil which have completely gelled, because of their lack of solubility, and results on the thickened oils cannot be accepted with complete confidence, due to certain limitations which are inherent in the methods of molecular weight determination The oils appear to be inclined to associate or dissociate in the solvents employed in the determination, and the degree to which association or dissociation occurs is different in the case of different solvents [13,14]

Regardless of the limitations of the methods, however, it appears obvious that no advanced degree of polymerization or association occurs up to the point of actual gelation No fractions have been isolated from the thickened products in a state of aggregation exceeding that of tetramers of the original oil, and in most cases the indicated molecular weight of the whole oil has approximated that of a dimer

The fatty acids recovered from polymerized oils by hydrolysis of the latter have in all cases consisted of monomeric and dimeric compounds [15]

The general tendency among drying oil chemists has been to consider the above mentioned dimers to be true chemical compounds, in which the two glyceride molecules are joined by primary valence forces This view, however, is not completely shared by all authorities on the subject, some of whom[3,16] are inclined to attribute the union between the two to physical association in the case of ordinary drying, and to admit the possibility of chemical combination only where the reaction is induced by heat

It is to be remembered, in connection with the molecular weight determinations, that only average values are obtained, and that minor proportions of polymers of high molecular weight may well escape detection by ordinary methods of fractionation and examination There is evidence that there may be some formation of high polymers near the beginning of the polymerization process Thus, for example, Lins,[17] employing an "ultrafiltration" method, noted an apparent formation of colloidal particles in linseed oil early in the heat bodying operation

The probable structure of drying oil gels has been likened by Kienle[18] to that of a "brush heap" or "log jam," in which a relatively small proportion of a highly developed polymer is intertwined and interlocked in such a manner as to hold enmeshed a relatively large proportion of liquid oil in a low state of polymerization It has been noted by Long and co

[14] A C Elm, *Ind Eng Chem*, 23, 881–887 (1931)

[15] J Marcusson, *Z angew Chem*, 39, 476–479 (1926)

[16] J S Long, A E Rheineck, and G L Ball Jr, *Ind Eng Chem*, 25, 1086–1091 (1933)

[17] K Lins, *Angew Chem*, 47, 564–568 (1934)

[18] R H Kienle, *J Soc Chem Ind*, 55, 229–237T (1936)

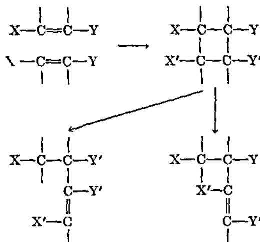
workers,[16,19] that well dried films may contain 70% or more of acetone-soluble oil

As pointed out by Bradley and Johnston,[20] the presence of liquid fractions in drying oil gels is not necessarily due to the polymerization being incomplete, but may rather be attributed to the production of heat altered esters which have lost their ability to intercombine, due to intramolecular cyclization, or other causes However, there is ample evidence that fresh gels are ordinarily in a state of polymerization considerably short of their potentialities in this respect There is apparently a progressive polymerization in paint films over a period of months or even years [16,19] Steger and van Loon[21] reported that gelation occurred in heat-treated tung and linseed oils when only 50% of their unsaturated acids had dimerized Bradley and Richardson[22] found 30% of the conjugated fatty acids of tung oil to be intact at the point of gelation

(c) Mechanism of Dimer Formation

The mechanism by which dimeric molecules of drying oils are formed has been a matter of much speculation Interest in the mechanism extends beyond the initial stage of polymerization inasmuch as the reaction which produces the dimer may conceivably extend to the formation of the larger aggregates which are assumed to exist in the gel or solidified paint film

It is generally agreed that polymerization proceeds through the medium of the double bonds existing within the fatty acid chains Morrell[3] has advanced the theory that linkage occurs through the temporary formation of an unstable four membered ring according to the following scheme:



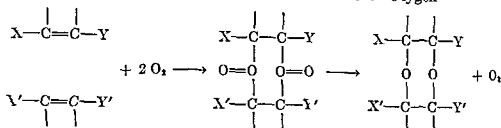
[19] J S Long, E K Zimmermann, and S C Nevins, *Ind Eng Chem*, 20, 806–809 (1928)

[20] T F Bradley and W B Johnston, *Ind Eng Chem*, 32, 802–809 (1940)

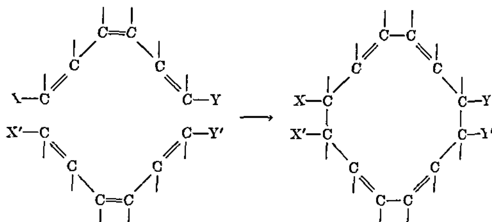
[21] A Steger and J van Loon, *Fettchem Umschau*, 43, 17–21 (1936)

[22] T F Bradley and D Richardson, *Ind Eng Chem*, 32, 963–969 (1940)

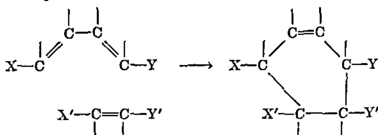
Marcusson[23] proposed a polymerization mechanism involving the development of a linkage through the medium of combined oxygen



Rossman[24] suggested that in the case of tung oil (elaeostearic acid glycerides) dimers were formed containing a twelve membered ring



The hypothesis of dimerization through the formation of a six membered ring by a Diels Alder[25] reaction was first proposed by Kappelmeier[26] The reaction is presumed to be as follows



It will be noted that the union of two fatty acid radicals by a Diels Alder reaction requires the presence of conjugated double bonds in one of the fatty acids Thus, in the case of nonconjugated oils, it is necessary to postulate a preliminary isomerization to yield double bonds in a conjugated position Such isomerization has been actually observed by a number of investigators

[23] J Marcusson *Z angew Chem* , 38, 780-782 (1925)

[24] E Rossmann *Fettchem Umschau* 40, 96-102 117-23 (1933)

[25] O Diels and K Alder *Ann* 460, 98-122 (1928)

[26] C P A Kappelmeier, *Farben Ztg* , 38, 1018-1020 1077-1079 (1933)

That conjugated acids are formed during the heat bodying of ordinary oils was first deduced by Scheiber[27] from the observation that the refractive index of linseed and similar oils increases during this operation, whereas that of tung oil decreases Scheiber's original observations were later elaborated into a theory of polymerization[28] which assumed this shifting of double bonds as the first step in the reaction

Evidence of a shift of double bonds to conjugated positions was noted by Taylor and Smull[29] in the case of heat-treated linseed oil, and by Steger and van Loon in purified ethyl linoleate [30]

Brod, France and Evans,[31] in an investigation of polymerization in the ethyl esters of the mixed 9,11- and 9,12-lineoleic esters in dehydrated castor oil, found that these two acids produced apparently identical polymers They considered this as evidence of isomerization of the ordinary 9,12 acid to the conjugated 9,11-form

A significant recent series of investigations of polymerization phenomena is that of Bradley and associates [20,22,32,37]

Bradley and Richardson[22] examined, by means of ultraviolet absorption spectra, samples of a number of different varieties of oil which had been heat-bodied at 575°F in sealed and evacuated tubes In the case of linseed oil, they found that heat treatment resulted in a progressive decrease in the linolenic acid content of the oil, accompanied by the appearance of conjugated acids The concentration of the latter reached a maximum estimated value of 4 8% There was also evidence of cyclization, both of monomeric and dimeric compounds The observations of Bradley and Richardson may be considered direct and positive evidence of the formation of conjugated acids, inasmuch as the physical method employed for their detection is not subject to the uncertainties involved in some of the previous investigations by chemical methods

Bradley and Johnston[20,35] subjected the methyl esters of various drying oils to heat treatment in an inert atmosphere, and reported a detailed

[27] J Scheiber, *Farbe u Lack*, **1929**, 585–587

[28] J Scheiber, *Farbe u Lack*, **1936**, 315–316, 329–330, 341, 351–352, *Fette u Seifen*, **43**, 103–105 (1936)

[29] R S Taylor and J G Smull, *Ind. Eng Chem* , **28**, 193–195 (1936)

[30] A Steger, J van Loon, and L N J van der Hulst, *Fettchem Umschau*, **42**, 217–219 (1935)

[31] J S Brod, W G France, and W L Evans, *Ind Eng Chem* , **31**, 114–118 (1939)

[32] T F Bradley, *Ind Eng Chem* , **29**, 579 584 (1937)

[33] T F Bradley, E L Kropa and W B Johnston, *Ind Eng Chem* , **29**, 1270–1276 (1937)

[34] T F Bradley, *Ind Eng Chem* , **30**, 689–696 (1938)

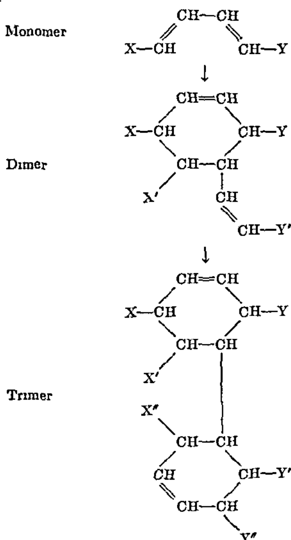
[35] T F Bradley and W B Johnston, *Ind Eng Chem* , **33**, 86–89 (1941)

[36] T F Bradley and H F Pfann *Ind Eng Chem* , **32**, 694–697 (1940)

[37] T F Bradley, *Ind Eng Chem* , **29**, 440–445 (1937)

examination of the reaction products, including a fractionation of the latter by means of molecular distillation

High yields of dimers were obtained (in some cases 60–70%), and also some trimers In all instances the evidence favored a cyclic structure in the polymers, apparently the latter were in some cases monocyclic and in others bicyclic It was concluded that cyclization consisted of the formation of six membered carbon rings, essentially according to the mechanism proposed by Kappelmeier The following scheme of trimer formation was proposed



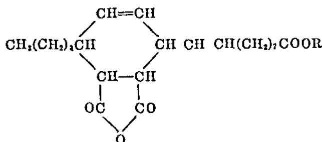
The rôle of oxidation in the polymerization of drying oils has been extensively investigated by Morrell and co workers[39–45] These investi

[38] N K Adam, R S Morrell, and H Samuels, *J Soc Chem Ind*, 53, 260–262T (1934)

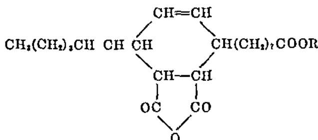
[39] R S Morrell and S Marks *J Oil Colour Chem Assoc*, 12, 183 205 (1929)

[40] R S Morrell and S Marks *J Soc Chem Ind* 50, 27–36T (1931)

gators have employed the glycerides of elaeostearic acid in the greater part of their work. When the alpha form of this acid is reacted with maleic anhydride, an addition product or "adduct" is formed which blocks the two double bonds farthest removed from the carboxyl group, leaving only the near linkage reactive. Similarly, in the adduct formed from the beta form of the acid, the two near linkages are blocked, leaving only the far double bond reactive.

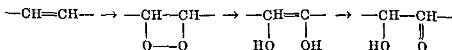


Alpha elaeostearic acid-maleic anhydride compound



Beta elaeostearic acid maleic anhydride compound

By working with the addition products rather than the simple glycerides, it is thus possible to study at will the reactions of either the near or the far bond. The experimental data have revealed that the three double bonds are by no means equivalent in reactivity. The middle (11 12) linkage is virtually inert toward atmospheric oxidation, consequently, it is considered that the first stage of oxygen addition involves the formation of peroxides at the other two bonds. Peroxides are formed at the near (9 10) bond with relative slowness and are inclined to isomerize to a hydroxy ketone group.



Oxidation takes place more readily at the far (13 14) group, and the peroxides formed at this position are more reactive than those formed at the

[42] R S Morrell and E O Phillips *J Soc Chem Ind*, **58**, 159 162T (1939)
[43] R S Morrell and E O Phillips, *Fette u Seifen* **46** 541-546 (1939)
[44] R S Morrell and H Samuels, *J Chem Soc*, **1932**, 2251 2254
[45] R S Morrell and W R Davis, *J Soc Chem Ind*, **55**, 237-246T, 261-267T (1936)

near bond It is through these latter, more reactive peroxides that polymerization takes place The beta elaeostearin compound polymerizes readily and forms hard, fast drying, varnish like films The alpha-elaeostearin compound polymerizes slowly and yields soft, slow drying films

(d) Miscellaneous Reactions in Bodying and Drying

In addition to the cyclization observed in the polymeric compounds formed in drying oils, there is considerable evidence of intramolecular rearrangement to form cyclic monomers Steger and van Loon[21] reported the presence of cyclic monomers in heat treated ethyl elaeostearate Bradley and Richardson[46] also found evidence of cyclization of monomers in various heat treated oils

Wolff and co workers[47,48] attributed the decreased hexabromide number of boiled linseed oil to the isomerization of linolenic acid to a form which gave soluble bromides Linoleic acid was also observed to isomerize to a high melting form with only one reactive double bond

That the polymerization of drying oils is not simply an addition process, but that it involves condensations and other reactions productive of low molecular weight compounds, is shown by the fact that carbon dioxide, volatile acids and water vapor are evolved, both in the bodying of oils under vacuum or nitrogen,[49] and in the drying of paint films [16]

That the drying of paint films is inhibited by moisture and is much retarded by a humid atmosphere was demonstrated by Schmutz and Palmer[50] and by Long, Rheineck, and Ball [16] Drying and polymerization are also inhibited by the presence of phosphatides[13] and other substances[51-53] which are effective as antioxidants in edible vegetable oils It is accelerated by metallic oxides, by sulfur and selenium and their oxides,[54,56] by heat, and by light [50,57]

The heat bodying of linseed oil and various synthetic triglycerides in the presence of oxygen was studied in detail by Long and Chataway[58] and

[46] T F Bradley and D Richardson *Ind Eng Chem*, 32 963 969 (1940)
[47] H Wolff and J Rabinovicz, *Fettchem Umschau*, 40 115-117 (1933)
[48] H Wolff and L Wallbaum *Fettchem Umschau*, 40, 113 115 (1933)
[49] J S Long, C A Knauss, and J G Smull, *Ind Eng Chem*, 19, 62-65 (1927)
[50] F C Schmutz and F C Palmer *Ind Eng Chem*, 22, 84-87 (1930)
[51] J Scheiber, *Angew Chem* 46, 643-647 (1933)
[52] A M Wagner and J C Brier, *Ind Eng Chem*, 23, 40-49 (1931)
[53] A M Wagner and J ([illegible]
[54] H I Waterman and C [illegible] T (1936)
[55] H I Waterman C [illegible] *m Ind*, 57, 87-89T (1938)
[56] However, sulfur and selenium inhibit the gelation of tung oil
[57] A de Waele *J Soc Chem Ind*, 39, 48-50T (1920)
[58] J S Long and H D Chataway, *Ind Eng Chem*, 23, 53 57 (1931)

Long and McCarter [59] At 100°C the rate of oxygen uptake was observed to be a straight line function of the degree of oxidation, up to the point of gelation The gelation point, in terms of oxygen absorbed, varied considerably with different oils, from approximately 5% (by weight) in the case of alpha-elaeostearin to 15% in the case of triolein Raw linseed oil gelled after taking up approximately 10% of oxygen, but heat bodied oil gelled with the absorption of less than 3% From 50% to 85% of the oxygen absorbed up to the point of gelation remained in the oil in a combined form The remainder formed volatile products of various kinds with 3 5% to 5% of the carbon and hydrogen of the oil In the case of linseed oil and also of triolein and trilinolenin, the amount of oxygen absorbed up to the point of gelation corresponded closely to that required to form one peroxide group per each molecule of unsaturated fatty acid

In oil drying, as in the oxidation of edible oils, the varied and complex reactions involved are obviously much influenced by such factors as temperature, rate of oxygen supply, concentration of oxidation products in the oxidizing atmosphere, the presence of pro or antioxidants, and the composition of the drying oils

"Frosting," or drying with the production of a wrinkled, folded surface is characteristic of films of conjugated acid oils This phenomenon is due to volume changes in the oil during the process of drying, their cause is obscure The tendency of films to frost is much enhanced by exposure to oven gases during baking Eibner and Rossmann [60] reported a microscopic examination of drying tung oil films They observed a shrinkage in volume, with the formation of small cracks, near the beginning of the drying period Later an expansion occurred, with the production of folds at right angles to the cracks Frosting of tung oil films is prevented by previous heat treatment of the oil or by the addition of certain dryers

Lately a considerable demand has arisen for wrinkle finishes, and alkyd enamels, etc , have been developed which produce a variety of novel effects through wrinkling The subject of wrinkling and wrinkle finishes is discussed in detail in a recent publication of Moore [61]

(e) *Deterioration of Paint and Varnish Films*

The failure of films of paint, varnish, etc , is apparently caused by reactions similar to those which lead to formation of the films It has been shown by Long, Rheineck, and Ball[16] and others, that paint films cease to absorb oxygen after a somewhat limited period The destruction of paint

[59] J S Long and W S W McCarter, *Ind Eng Chem* , **23**, 786–791 (1931)

[60] A Eibner and E Rossmann, *Chem Umschau Fette, Öle, Wachse Harze*, **35**, 281–290 (1928)

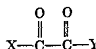
[61] H R Moore, in *Protective and Decorative Coatings* Vol III, edited by J J Mattiello, Wiley, New York, 1943, pp 250–266

films is, therefore, not due to oxidation as such, but rather to a too advanced degree of polymerization So long as the paint retains a sufficient amount of liquid oil to act as a plasticizer it remains tough and flexible After the liquid portions have largely polymerized to a solid form, however, the film becomes brittle and readily cracks and peels away A similar cracking occurs in varnished surfaces but with a lesser tendency for the film to become nonadherent

In the ideal drying oil, therefore, the first or the "drying stage" of polymerization will be short, the second or "deteriorative stage" will be prolonged Although various means may be employed for accelerating the drying process, opportunity for inhibiting later polymerization is limited To some extent late polymerization may be minimized by properly balancing the relative proportions of reactive and nonreactive fatty acids in the oil The popularity of linseed oil as a drying oil in the past is attributed to its desirable balance in this respect In varnishes and other heat treated products the cooking operation may produce nonreactive, plasticizing compounds, as mentioned previously

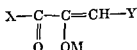
A phenomenon of considerable practical significance in the deterioration of oil films is that of "yellowing" The tendency of oil films to develop a yellow or brownish color with age is in more or less direct proportion to their degree of unsaturation Oils which contain little of any fatty acids more unsaturated than linoleic (soybean oil, poppyseed oil, dehydrated castor oil, etc), are relatively free from this defect It is, of course, most noticeable in white paints and enamels, and is favored by the presence of basic pigments

It appears to be generally agreed that yellowing is in some way connected with the presence of keto groups in adjacent positions in the fatty acid chain



Such a group is in itself chromophoric, Elm and Standen[62] proved by synthesis of the respective compounds that diketostearic acid is yellow, whereas ketohydroxystearic acid is colorless

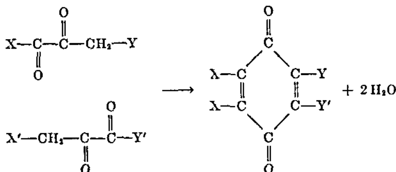
According to the views of Morrell and Phillips,[63] the yellow substance is probably a metallic compound formed from the diketone, of the formula



where M may be any basic substance as for example, a basic pigment

[62] A C Elm and G W Standen *Ind Eng Chem* 24, 1044 1045 (1932)
[63] R S Morrell and E O Phillips *Fette u Seifen*, 46, 541 546 (1939)

More recently, Prill[64] and O'Daniel and Parsons[65] have demonstrated that diketones occur in partially oxidized nondrying fats containing fatty acids more unsaturated than oleic, and that these compounds may be estimated by means of the yellow color which they develop upon treatment with an alkali The color in this case is attributed to quinoid compounds formed by an aldol condensation of two diketone molecules·



A somewhat similar mechanism may be operative in the yellowing of paint films

Yellowing does not occur in a perfectly dry atmosphere or at low temperatures [66] It cannot be due to impurities in the oil, as pure trilinolenin yellows badly [14, 66] It is favored by irradiation from the red portion of the visible spectrum, but is prevented by exposure to ultraviolet light,[66] hence is chiefly noticeable in white or light colored interior finishes

(f) Concept of Functionality in Oil Drying

Certain aspects of the phenomenon of oil drying have been greatly clarified by the concept of functionality in polymerization, as developed by Carothers[67, 68] and Kienle and co workers,[69-74] through their researches on synthetic resins, and applied specifically to drying oils by Bradley [34, 37]

According to the theory developed on the basis of this concept, the reactions occurring in polymerization are not to be regarded as necessarily different from those occurring between ordinary organic compounds The distinguishing feature of polymerization is rather the peculiar multiplicity of these reactions

[64] E A Prill, *Oil & Soap*, 19, 107–109 (1942)
[65] L O'Daniel and L B Parsons *Oil & Soap*, 20, 72 74 (1943)
[66] S Werthan A C Elm, and R H Wien, *Ind Eng Chem*, 22, 772–776 (1930)
[67] W H Carothers, *J Am Chem Soc*, 51, 2548–2559 (1929)
[68] W H Carothers and J A Arvin *J Am Chem Soc*, 51, 2560–2570 (1929)
[69] R H Kienle, *Ind Eng Chem*, 22, 590–594 (1930)
[70] R H Kienle *Ind Eng Chem* 23, 1260–1261 (1931)
[71] R H Kienle and P F Schlingman, *Ind Eng Chem*, 25, 971–975 (1933)
[72] R H Kienle and C S Ferguson, *Ind Eng Chem*, 21, 349–352 (1929)
[73] R H Kienle and A G Hovey, *J Am Chem Soc* 51, 509–519 (1929)
[74] R H Kienle and A G Hovey, *J Am Chem Soc*, 52, 3636–3645 (1930)

In the molecules of the polymerizable substance, the groups which are reactive or capable of uniting to form polymers are termed "functional." Compounds containing one such group are "monofunctional," those which have two functional groups are termed "bifunctional," etc.

For a compound to be capable of attaining a high degree of polymerization, it must be at least bifunctional. Two monofunctional molecules are incapable of further reaction after they have united to form a dimer, since all of the functional groups will have disappeared in bringing about their union. In the case of bifunctional compounds, the dimer will retain the same degree of functionality as the unpolymerized compound. One functional group from each molecule will disappear in the reaction, but the remaining two groups will remain free, to give the dimer resulting from their union a functionality of two. In each succeeding reaction a new functional group will be added to the polymer for each group that disappears, so that the polymer will continue to be bifunctional, regardless of how far polymerization is carried, unless ring closure occurs to reduce the functionality to zero. Bifunctional compounds are capable of continued linear growth, but cannot assume the three dimensional, interlocked structure of solid polymers. Linear polymers are in general, liquid, fusible, and soluble in ordinary solvents.

If the compound in question has a functionality of three or more, a highly significant situation arises. Then there will be a progressive increase in the functionality of the polymer, as polymerization proceeds. Thus a trifunctional compound will possess a functionality of four at the dimeric stage, five at the trimeric stage, six at the tetrameric stage, etc. In other words, at each successively advanced degree of polymerization the polymer becomes more reactive and more capable of further molecular growth in all directions. In such compounds, polymerization rapidly results in three dimensional cross bridging between adjacent molecular chains to form a rigid, lattice like structure. Polymers of this structure are solid, infusible, and insoluble in ordinary organic liquids.

Upon the basis of the functionality of the reacting compounds, polymerization reactions are subject to mathematical treatment leading to prediction of the degree of polymerization at which the three dimensional structure will appear. Such treatments have been given by Carothers,[75] Kienle[18] and Flory.[75a]

It has been frequently observed in the past[37, 76, 78] that triglycerides of

[75] W. H. Carothers, *Trans. Faraday Soc.*, 32, 39–53 (1936).
[75a] P. J. Flory, *J. Am. Chem. Soc.*, 63, 3083–3100 (1941).
[76] A. Y. Drinberg and A. A. Blagonravova, *Natl. Paint, Varnish Lacquer Assoc. Circ.* No. 501, 21–30 (1936).
[77] E. Fonrobert and F. Pallauf, *Chem. Umschau Fette, Öle, Wachse Harze*, 33, 41–51 (1926).
[78] R. S. Morrell, *J. Oil Colour Chem. Assoc.*, 7, 153–164 (1924).

unsaturated acids are peculiarly subject to drying or polymerization, as compared with the free acids, their mono or diglycerides, or their esters with mono- or dihydric alcohols. On the other hand, the esters of fatty acids and polyhydric alcohols with more than three hydroxyl groups (such as erythritol or mannitol) dry or polymerize even more readily than the corresponding acids combined with glycerol.[58,76] While fatty acids and their mono or di esters will exhibit some degree of gelation with prolonged heat treatment[59] and can be made to form soft, tacky films, combination of the fatty acids with glycerol or a higher polyhydric alcohol is requisite for the production of films which are infusible and insoluble, and truly hard and serviceable.

The preceding observations are readily interpreted in the light of the functionality theory. Apparently each unsaturated fatty acid radical in a drying oil has normally a functionality of but one. Therefore, the fatty acids must be esterified with an alcohol with at least three hydroxyl groups in order for the resulting ester to have a sufficient functionality to be capable of forming three-dimensional polymers.

While the functionality theory of polymerization was developed upon the assumption of actual chemical reaction between the polymerizing molecules, it is to be noted that it is actually independent of the mechanism of molecular union. It is not only applicable to polymerization by either addition or condensation, but is also equally valid if molecular aggregation occurs through the medium of polar groups as postulated by Long and his associates,[16] or by other physical, rather than chemical means.

3. Refining of Drying Oils

For the production of the highest grade varnish oils, drying oils are generally refined with caustic soda, by a process similar to that employed in the manufacture of edible oil products. Alkali refining completely removes the free fatty acids present in the crude oil, removes all phosphatides and mucilaginous materials, and also produces a lighter colored oil than other methods of refining. It is a relatively expensive treatment, however, as it involves a considerable refining loss.

In drying oils which are destined for the manufacture of paints rather than varnishes, the free fatty acids which are naturally present in crude oils are rarely objectionable. In fact, in some products a considerable free fatty acid content in the oil is actually desirable. In paints which contain basic metallic pigments there will be some degree of reaction between the pigments and the free fatty acids of the oil, which will produce a coating of metal soaps upon the surface of the pigment particles. This coating is an aid to the wetting of the pigment in the grinding process. It promotes dispersion of the pigment and inhibits flocculation and settling in the finished paste or paint.

On the other hand, the presence of phosphatides and mucilaginous materials is objectionable in all drying oils Oils containing these substances "break" when heated rapidly to 550° to 600°F, i e, they deposit their impurities in the form of flocculent particles The presence of "break material" is, therefore, inadmissible in any oil which is to be heat bodied The presence of "break materials" in a paint film also appears to have a deleterious effect upon the durability of the film, due to their tendency to wash out under the influence of the weather In addition, they function as antioxidants and retard the drying of the oil

In the refining of paint oils the primary object, therefore, is the removal of "break material" The prolonged storage and settling of the oil in open tanks results in its fairly efficient removal Most of this material, particularly that of a phosphatidic nature, becomes insoluble through hydration, which will in time occur through the absorption of moisture from the air It is quite common practice, however, to accelerate the process of hydration by steaming the oil The colloidally dispersed "break material," as mentioned before, may be coagulated and precipitated simply by the application of heat Some of the commercial processes combine steaming and heating in one operation, usually under a vacuum In this case the process bears some resemblance to ordinary steam deodorization of edible oils

Where chemical treatment other then alkali refining is resorted to for the removal of "break material" in paint oils, the usual refining agent is strong sulfuric acid, which properly used, dehydrates and precipitates the impurities without any considerable action upon the oil itself

Both linseed and soybean oils which are intended for paint and varnish manufacture are quite commonly "refrigerated," i e, artificially chilled and filtered for the removal of traces of dissolved waxes The removal of waxes is said to be particularly important if the oil is to be used in baked finishes, which are otherwise subject to pitting

The bleaching of drying oils is almost invariably accomplished by means of a bleaching earth, preferably of the acid activated type, with or without the accessory use of a bleaching carbon Bleaching of paint and varnish oils by chemical agents is not considered good practice because of the deleterious effect of such agents upon the glycerides of the oil

Fish oil is almost invariably heat-treated before it is used in paints, to improve its drying properties and to destroy its fishy odor Fish oil is normally somewhat higher in free fatty acid content than crude vegetable oils, and is usually alkali refined for use in paints and allied products It must also be refrigerated or "cold cleared," not for the removal of waxes, but for the removal of "stearine" or solid glycerides, before it is in a suitable form for use in paints or varnishes The character of the films formed by fish oil depends to a large extent upon the thoroughness with which the

refrigeration process is carried out Fish oil paints are in general inclined to be soft and tacky, due to the high content of saturated fatty acids in the oil Careful refrigeration to remove the bulk of the more highly unsaturated glycerides will effect a marked improvement in the hardness of the films

4 Unmodified Drying Oils

There is a considerable use in the paint and varnish industry of unmodified drying oils, which may be defined as oils whose glycerides are essentially unaltered by processing treatment Unmodified oils may be treated for the removal of nonoil impurities, or may have dryers added, but are to be distinguished from oxidized, polymerized, and other modified oils which have undergone treatment which involves actual reaction of their glycerides

Raw linseed oil, and to a lesser extent soybean and other oils, are extensively used in paints and vehicles for the wet grinding of pigments

Raw grinding oils are generally acid refined and bleached The lighter grades of linseed oil, which are in demand as vehicles for pigments of the lightest and most delicate shades, may have Lovibond colors as low as 20 yellow and 2 0 red, although the color of most grinding oil is in the neighborhood of 35 yellow and about 6 0 red Soybean grinding oils are generally slightly lighter in color than linseed oil

The free fatty acid content of grinding oils is somewhat variable An extremely low acidity in the oil is for most purposes considered neither necessary or desirable A certain degree of reaction between the pigments and the free acids will produce a coating of metallic soaps upon the pigment particles, which aids in wetting the pigment and maintaining it in a dispersed condition On the other hand, excessive reactivity between the pigment and the oil may cause livering in the paint The optimum degree of acidity in the oil depends upon the reactivity of the pigment Oils of low acidity, with an acid value of 1 to 2, are preferred for grinding zinc oxide and lithopones Oils for grinding white lead pastes may have acid values as high as 12 to 16 The acid value of average grinding oils is between about 4 and 6

The oils used for compounding with pastes and thinners, for the production of mixed paints, include both raw and boiled oils A boiled oil is, properly speaking, simply a drying oil, usually linseed oil, into which has been incorporated a metallic "dryer"

The metals which are most suitable and most commonly used in the preparation of dryers are lead, cobalt, and manganese Each of these three metals is more or less distinctive in its action, consequently, in order to obtain the most desirable drying effect, different dryers are often used in combination The action of dryers appears to be quite similar to that

of metallic pro oxidants in nondrying oils In other words, they increase the rate of oxidation of the oil, probably in part through their destructive effect on the antioxidants naturally present in the oil

Formerly the common practice in the preparation of boiled oils was to add the dryer metals in the form of their oxides, and then heat the oil in an open kettle to a temperature of 500° to 550°F until the oxides were dissolved, through the action of the fatty acids in the oil Since this operation required several hours time, a considerable amount of oxidation and heat polymerization also occurred in the process

In modern practice, soluble soaps of the dryer metals are prepared separately from the oil They are then blended with the oil while the latter is maintained at a temperature only high enough to insure thorough solution and dispersion of the dryer (usually 225° to 250°F) When "boiling" is conducted by this procedure, oxidation and polymerization ordinarily occur only to a negligible extent, although, if desired, some degree of oxidation or heat bodying may be obtained by raising the temperature or blowing the oil with air

The three principal classes of soluble metallic dryers are resinates, linoleates, and naphthenates They are prepared by reacting metallic oxides or salts with the mixed fatty acids of rosin, the mixed acids of a drying oil, or naphthenic acid, respectively, or by reacting the sodium soaps of the acids with a salt of the metal Cobalt is a very powerful dryer and is not usually used in a concentration of more than about 0 05% Manganese is less active than cobalt, and if used alone may be added to the extent of 0 1–0 2% (on the basis of the metal) Lead is the least active of the three metals, and is often used to the extent of as much as 0 5% of the oil

Commercial boiled linseed oils usually have a drying time of 12 to 18 hours, as compared with about 72 hours or raw oil, although special grades are marketed with drying times as low as 4 hours The color of the oil increases somewhat in boiling and is usually above 35 yellow and 10 0 red, although special light boiled oils are available which are as light as 35 yellow, 6 0 red The acid value of the oil increases slightly in boiling, but is not usually greater than about 6 in the finished product In oils boiled by modern methods there is only a slight increase in the density or the viscosity of the oil

In the preparation of boiled fish oils it is customary to subject the oil to a somewhat higher temperature, and some degree of oxidation, in order to free the oil of its characteristic fishy odor

Varnish and enamel oils, unlike those destined for use in paints, are almost invariably alkali refined, to produce a low acidity in the oil For most purposes it is desirable for these oils to be completely neutral, although a moderately low acid value (1 to 3) is sometimes preferred for

special purposes, as for example, where the oil is to be compounded with certain synthetic resins

5. Modified Drying Oils

(a) *Heat Polymerized Oils*

Heat-polymerized drying oils, or "stand oils," are extensively used in the manufacture of varnishes, enamels, printing inks, and lithographic varnishes, and are also used to some extent in paints, for the gloss and leveling properties that they contribute

In the older heat polymerization processes, in which the oil was heated in open, direct fired kettles, the oil underwent a considerable amount of oxidation In modern practice, drying oils are often heat bodied without

TABLE 125
COMPARISON BETWEEN VISCOSITIES ON THE GARDNER HOLDT SCALE AND ABSOLUTE VISCOSITIES

Gardner Holdt viscosity	Absolute viscosity poises	Gardner Holdt viscosity	Absolute viscosity poises
A	0 50	Q	4 35
B	0 65	R	4 70
C	0 85	S	5 00
D	1 00	T	5 50
E	1 25	U	6 27
F	1 40	V	8 84
G	1 65	W	10 70
H	2 00	X	12 9
I	2 25	Y	17 6
J	2 50	Z	22 7
K	2 75	Z 1	27 0
L	3 00	Z 2	36 2
M	3 20	Z 3	46 3
N	3 40	Z-4	63 4
O	3 70	Z 5	98 5
P	4 00	Z 6	148 0

access to the air, either under a vacuum or underneath the protection of an atmosphere of carbon dioxide or other inert gas Oils so bodied are light in color and low in acidity, and are said to be particularly superior to the older stand oils in their resistance to moisture in the applied films Heat bodying accompanied by oxidation apparently produces greater amounts of hydrophilic substances in the oil than does bodying without access to air

During the heat bodying process, polymerization is controlled by means of viscosity determinations on the oil For ordinary analytical and control purposes, viscosity is determined by the air-bubble method at 25°C (77°F) against a standard set of Gardner-Holdt tubes[79] and expressed on the

[79] H A Gardner, *Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors* 9th ed, Institute of Paint and Varnish Research, Washington, 1939

Gardner Holdt scale The relationship between Gardner Holdt viscosities and viscosity in absolute units is shown in Table 125

Oils may be bodied to any viscosity up to near gelation, according to their anticipated use Accompanying the change in viscosity during bodying are alterations in the iodine value, acidity, refractive index, saponification value, specific gravity, acetyl or hydroxyl value, etc Some of these alterations are the natural result of polymerization, others are due to the accumulation of heat degradation products For detailed information relative to the effect of heat polymerization on the physical and chemical characteristics of different oils, the reader is referred to the original publications of Caldwell and Mattiello[79a] (linseed oil), Sorenson, *et al* [79b] (tung and oiticica oil), Gerkens and Kildare[80] and Von Mikusch[81] (dehydrated castor oil) Work *et al* [82] (menhaden oil), and the Los Angeles Paint and Varnish Production Club[83] (sardine oil) Although there is some tendency for oils to increase in acidity during heat bodying, it is possible to produce a high viscosity product from alkali refined linseed oil, with an acid value not greater than about 3–4 There is little tendency for tung oil to become *more acid during heat bodying* *Bodied linseed oil with a Gardner Holdt* viscosity of Z-4 is produced commercially with a Lovibond color no greater than 35 yellow, 3 0 red

In the bodying of oils for inclusion in pigmented products, the character and general desirability of the oil is not determined exclusively by its viscosity, but is also influenced to some extent by the conditions under which bodying is carried out The reason for this is that oils processed at different temperatures and with different degrees of oxidation will vary in their surface active properties, even though their viscosities may be the same Consequently, they will wet and deflocculate or flocculate the pigments to different degrees, with consequent effect on the physical properties of the product The relationship *between processing conditions* in oil bodying and wetting in pastes prepared from the bodied oils and various pigments, has been the subject of an extensive investigation by Mattiello and Work [84] See also General References, page 366

[79a] B P Caldwell and J Mattiello *Ind Eng Chem*, 24, 158 162 (1932)

[79b] S O Sorenson C J Schumann J H Schumann, and J J Mattiello *Ind Eng Chem* 30, 211 215 (1938)

[80] J F ([illegible] *Coatings* Vol III, ed [illegible]

[81] J D [illegible]

[82] L T [illegible] *Chem*, 28, 1022 1024 (1936)

[83] Los Angeles Paint and Varnish Production Club *Natl Paint Varnish Lacquer Assoc Circ* No 546, 263 271 (1937), *Am Paint J* 22 22 24 (Oct 30 1937)

[84] J J Mattiello and L T Work *Natl Paint, Varnish Lacquer Assoc Circ* No 502, 31 138 (1936) In this connection see also the discussion of heat bodying in relation to wetting of pigments by J J Mattiello, in *Protective and Decorative Coatings*, Vol III, Wiley, New York 1943 pp 45–86

In addition to the conventional methods of batch polymerization by heat, a number of special methods have been proposed for effecting polymerization more rapidly or conveniently Among these may be mentioned the following The continuous "thermolyzing" process of Reece,[85] which involves rapidly heating tung oil or other oil to a higher temperature than is employed in batch polymerization, e g, to 625°F, and then quickly cooling the oil before there has been time for gel formation, the "voltolizing" process[86] for producing solid polymers by an electrical discharge, and other processes depending upon electrical effects, such as the cathode ray method of Long[87], chemical processes depending upon the addition of finely divided metals, sulfur, sulfur dioxide, boron compounds, etc, and processes depending upon the application of very high pressures[88 89] It may be mentioned that the polymerization of tung oil at temperatures as low as 50°C (122°F) has been reported by Starkweather[90] The pressures employed in this instance were of the order of 500 to 6000 atmospheres

The above and other special methods of polymerization are reviewed in a recent publication of Rheineck[91]

For detailed information on the technology of polymerization, including descriptions of the process as carried out commercially, and data on the response of different oils to heat bodying, see the later chapter devoted to polymerization and related processes (687–699)

(b) *Blown or Oxidized Oils*

Blown or oxidized oils are prepared by aerating drying oils at a temperature of 200–250°F, for several hours As oxidation progresses, the viscosity of the oil rises, as in heat bodying, and the specific gravity increases, approaching a value of 1 0 in the heavier blown oils

Since blown oils have many of the characteristics of heat polymerized oils, but are processed at temperatures within the range of ordinary steam heating, blowing represents a cheap and relatively easy method of increasing the body of an oil However, blown oils produce less resistant films than heat bodied oils, due to their greater content of hydroxyl groups, etc

[85] F M Reece, U S Pat 1,903,686 (1933) F M Reece and M F Taggart, U S Pat 2,113 358 (1938)

[86] L Hock and C L Nottebohm, *Kolloidchem Beihefte* 31, 185–221 (1930)

[87] J S Long (one third to Lehigh Univ and one third to Archer Daniels Midland Co and W O Goodrich Co), U S Pat 1 818,073 (1931)

[88] E W Fawcett R O Gibson and M W Perrin (to Imperial Chemical Industries Ltd), U S Pat 2 155 009 (1939)

[89] J L Schneider, S L Flugge, and R J Evans (to Continental Can Co), U S Pat 2 120 044 (1938)

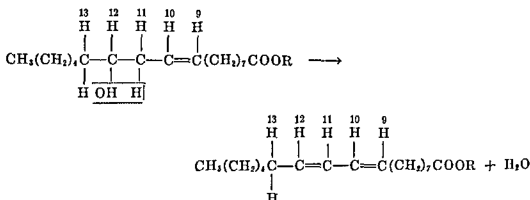
[90] H W Starkweather *J Am Chem Soc*, 56, 1870–1874 (1934)

[91] A E Rheineck, in *Protective and Decorative Coatings* Vol III, edited by J J, Mattiello, Wiley, New York, 1943, pp 29–44

Also, their solubility in mineral spirits and other solvents is limited For some purposes the properties of blown oils are unobjectionable, or even desirable Because of their high *surface activity*, blown oils are sometimes valuable for mixing with other oils to promote pigment wetting in paints and enamels They are also used in the manufacture of *oilcloth*, *patent leather*, oiled fabrics, and lithographic varnishes, especially the heavier grades of the latter Blown oils are generally somewhat darker in color and higher in free fatty acid content than heat polymerized oils of equivalent viscosity

(c) *Dehydrated Castor Oil*

The dehydration of castor oil depends upon the removal of the hydroxyl group and an adjacent hydrogen atom from ricinoleic acid, in the form of water, to form 9 10, 11 12 octadecadienoic acid



This acid has conjugated double bonds and thus is similar to the elaeostearic acid of tung oil except that it contains two, rather than three double bonds Dehydrated castor oil has, therefore, to a considerable extent the properties of tung oil

It is also possible for dehydration to take place by removal of hydrogen from the 13th carbon atom rather than the 11th, as indicated above to form ordinary 9 10, 12 13 linoleic acid Priest and Von Mikusch[9] have made a careful study of the composition of various laboratory and commercially prepared samples of dehydrated oil Contrary to the claims of Scheiber,[93] they conclude that dehydration is never complete (there is always a residue of hydroxy acids), and that in all cases the production of unconjugated linoleic acid considerably exceeds that of the conjugated form Analyses of various samples of both unbodied and bodied dehydrated oils, as well as dehydrated castor oil acids, as reported by these

Ind Eng Chem 32, 1314 1319 (1940)
4, 1930, 513–514 524–525
309 (1930) 513 540 (1930),
5 (1934), 1 942,778 (1934)

TABLE 126

ANALYSIS OF DEHYDRATED CASTOR OILS AND FATTY ACIDS[a]

Analysis	Oil[b]								
	A	B	C	D	E	F	G	H	I
Acid value	1 8	2 6	4 4	13 1	17 0	1 55	3 4	4 8	195 9
Saponification value	190 4	190 0	192 7	190 9	191 2	192 0	191 9	191 6	197 3
Iodine value (Hanus)	155 5	147 1	143 8	157 0	152 9	—	—	—	165 2
Iodine value (Wijs)	141 2	—	—	145 8	—	137 6	117 9	115 1	153 0
Diene value (Kaufmann)	21 4	15 4	15 5	21 9	17 8	17 6	12 7	12 7	26 5
Acetyl value	13 5	14 3	24 8	16 1	19 1	10 6	6 7	9 2	1 2
Viscosity (Gardner)	F G	H	K	E-F	P	M	Z3	Z2 73	A
Color (Hellige)	1 2L	1	2-3L	2L	1 2L	2L	2L 2	1L 1	12Y 1 3R[c]
Specific gravity at 25°C	0 9305	0 935	—	—	—	0 9365	0 9505	—	0 903
Hexabromide value	0 0	—	—	—	—	—	—	—	0 0
Moisture, %	0 0	—	—	—	—	0 0	0 0	—	0 45

[a] G W Priest and J D Von Mikusch, *Ind Eng Chem* , 32, 1314–1319 (1940)

[b] A = typical analysis of a raw dehydrated castor oil made directly from castor oil, type 1, B = sample of a raw dehydrated castor oil, type 2, C = sample of a raw dehydrated castor oil, type 3, D = sample made in laboratory according to Münzel's patent, E = sample of European oil made by Scheiber process, type 4, F = typical analysis of a varnish oil (slightly bodied) made from raw oil of type 1, G = typical sample of a heavy bodied oil made from raw oil of type 1, H = sample of heavy bodied oil of different origin, type 5, I = typical sample of a distilled fatty acid made commercially for the manufacture of alkyd resins from raw oil of type 1

[c] Lovibond color

authors, are detailed in Table 126 From this analytical data, they estimate the composition of dehydrated castor oil, in comparison with ordinary castor oil, to be as indicated in Table 127

In many of its properties, such as drying time, rate of polymerization when heated, and resistance to water and alkalies in varnish films, dehydrated castor oil is intermediate between linseed oil and tung oil It is said to produce films which are softer than those of linseed, perilla or tung oils, but of superior elasticity. Because of its lack of triply unsaturated acids, its resistance to yellowing is outstanding The properties of dehydrated castor oil, in comparison with various natural drying oils, are discussed at length by Priest and Von Mikusch [94]

Dehydrated castor oil has attained extensive use as a replacement for tung oil in the manufacture of quick-drying and water resistant varnishes and enamels It has also been used to some extent in most other varieties

TABLE 127

COMPOSITION OF COMMERCIAL DEHYDRATED CASTOR OIL, IN COMPARISON WITH THE ORIGINAL OIL[a]

	Castor oil[b]	Dehydrated oil
Saturated acids %	0 3	0 5- 2 5
Hydroxy acids, %	87 8	3 -8
Oleic acid, %	7 2	7 5-10 5
9 10, 12 13 Linoleic acid, %	3 6	59 -64
9 10, 11 12 Linoleic acid, %	0	17 -26

[a] G W Priest and J D von Mikusch, *Ind Eng Chem*, 32, 1314-1319 (1940)
[b] Composition as reported by H K Dean, *Utilization of Fats*, Chemical Pub Co, New York, 1938

of drying oil products, including paints, oiled fabrics, linoleum, patent leather, and printing inks and lithographic varnishes

All of the dehydrated castor oil produced in the United States is apparently made by some variation of the Ufer process,[95] rather than by the original method of Scheiber,[93] *i e*, dehydration is carried out on the glycerides rather than the separated fatty acids of the oil It is marketed under the trade names of Isoline, Synthenol, Dehydrol, Castung, Kastolene, etc

Castor oil dehydrated by the Munzel process,[96] which involves both dehydration and dehydrogenation, is said to contain a triply unsaturated conjugated acid, with double bonds in the 9·10, 11 12, and 13.14 positions, respectively This oil has been produced commercially in Europe, under the trade name of Trienol According to Blom,[97] this product will

[94] G W Priest and J D Von Mikusch, in *Protective and Decorative Coatings* Vol I, edited by J J Mattiello, Wiley, New York, 1941, pp 115-150
[95] H Ufer (to I G Farbenindustrie), Ger Pats 529,557 (1931), 561,290 (1932), U.S Pat 1,892,258 (1932)
[96] F Münzel, Swiss Pat 193,931 (1938)
[97] A V Blom, in Oil and Colour Chemists' Assoc, *Varnish Making* Chemical Pub Co, New York, 1940, pp 31-39

gel in 1 5 minutes at 280°C (536°F), and dries more rapidly than natural tung oil However American workers[97] have been unable to substantiate the claims of some of the Munzel patents

(d) Isomerized Oils

The isomerized oils which have recently appeared on the market in the United States under the trade names of Conjusoy, Conjulin, etc , are prepared by treating oils containing linoleic and linolenic acids in such a

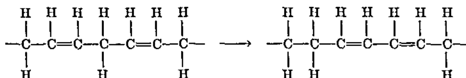
TABLE 128

CHARACTERISTICS OF ISOMERIZED DRYING OILS[a]

Characterist c	Soybean oil	Linseed oil product No 1	Linseed oil product No 2
Viscosity (Gardner Holdt)	Z 3	Z 6	Z 3
Acid value	5 9	12 9	8–12
Specific gravity at 25°C	0 9427	—	—
Diene value (Ellis-Jones)	17 4	—	—
Color, Hellige	—	2 3L	—
Browne heat test (gelation time)			
at 540°F , min	—	34	13–16
at 600°F , min	20	12	6 5–8 5

[a] *Woburn Chemical Corp* (N J), Bull No 121 (1941)

manner as to induce a shift in the double bonds of these acids to conjugated positions



These oils, like dehydrated castor oil, are substitutes for tung oil

Apparently, the isomerized oils so far produced are made from soybean and linseed oils by the alkali isomerization process described by Bradley and Richardson[98] This process consists essentially of reacting the fatty acids of the oil with an excess of aqueous alkali solution at a high temperature (425–450°F) and a correspondingly elevated pressure, acidulating the resulting soap to recover the isomerized acids, and reesterifying the latter with glycerol Laboratory isomerization of soybean oil by this method produced simultaneous yields of doubly and triply unsaturated conjugated acids as high as 43 8% and 2 2%, respectively, as estimated from ultraviolet absorption spectra data Corresponding yields of these acids from laboratory isomerized linseed oil were as high as 35 2% and 9 7%, respectively

[98] T F Bradley and D Richardson, *Ind Eng Chem* , 34, 237-242 (1942)

Novel products with a very high capacity for polymerization are produced by substituting for glycerol a polyhydroxy alcohol such as pentaerythritol, but so far these do not appear to have been made commercially

The isomerized oils are sold in a bodied form, some degree of heat polymerization presumably being unavoidable in the process of re esterification The characteristics listed in Table 128 are reported by one manufacturer of these materials[99]

The isomerized oils, as compared with other drying oils, are somewhat slower in drying, and form softer films than might be expected from their content of conjugated acids, which greatly exceeds that of dehydrated castor oil It is believed this is due to the formation of isomers such as 10 11, 12 13 acids, and 10 11, 12 13, 14 15 acids, which polymerize less readily than 9 10, 11 12 or 9 10, 11 12, 13 14 acids However, the isomerized soybean oil manufactured at present is roughly equivalent to dehydrated castor oil in drying properties, and isomerized linseed oil is superior to dehydrated castor oil, although inferior to tung oil The water resistance of isomerized linseed oil films has been reported to be higher than those of tung oil,[100] although their alkali resistance is less than that of tung oil films

(e) *Fractionated Oils*

There has recently been much interest in fractionation processes for the improvement of oils with poor drying properties Oils such as soybean oil and fish oils contain large proportions of highly unsaturated acids containing two or more double bonds, but are prevented from drying readily to form hard nontacky films, by the presence of considerable amounts of glycerides of saturated and monounsaturated acids Removal of the latter converts these oils to products comparable to highly unsaturated vegetable oils, such as perilla oil or linseed oil of high iodine value Fractionated oils are to be distinguished from isomerized oils, however, as they do not contain conjugated fatty acids

Fractionation for the improvement of drying properties may be carried out either upon the oil or its separated fatty acids In the latter case, the fatty acids must of course be re-esterified with glycerol or other polyhydric alcohol

Fish oils, such as sardine or menhaden, are particularly suitable materials for fatty acid fractionation, since most of their saturated fatty acids contain 14 to 16 carbon atoms, whereas their highly unsaturated acids containing three or more double bonds per molecule, are principally C_{20} and C_{22} acids An excellent separation of the two classes of acids may be obtained by fractional distillation Some improvement in the drying

[99] *Woburn Chemical Corp*, (N J), Bull No 121 (1941)

[100] J E *Good, Can Paint & Varnish Mag*, 17, 5, 7, 17, 23, 25 (Feb, 1943)

properties of soybean or other vegetable oils may be effected by the same process since the saturated acids of these oils consist principally of palmitic (C_{16}) acid, which is more volatile than the unsaturated C_{18} acids

Fractionated soybean oil and fish oil fatty acids, as well as different grades of triglycerides from fractionated fish oil acids, have been placed on the market by one American manufacturer under the trade name of "Neo Fats" Characteristics of some of these products, as reported by the manufacturers,[101] are listed in Table 129 The manufacture of these products

TABLE 129

CHARACTERISTICS OF NEO FATS (PRODUCTS OF FATTY ACIDS FRACTIONATED BY DISTILLATION)[a]

Number	23	19	170	190
Type	Fatty acids	Fatty acids	Triglyceride	Triglyceride
Source	Soybean oil	Fish oils	Fish oils	Fish oils
Mean molecular weight	280 0	305 0	—	—
Neutralization value	201 0	184 0	—	—
Saponification value	—	—	160 0	177 0
Iodine value Wijs	145 0	235 0	170 0	205 0
Acid value	—	—	8 0	6 0
Titer, °C	21 0	20 0	—	—
Specific gravity at 25°C	—	—	0 980	0 950
Viscosity at 25°C poises	—	—	heavy	2 0
Unsaponifiable matter, %	0 3	0 5	—	—
Color	nil	pale	dark	pale
Odor	mild	good	—	—
Approximate composition of fatty acids, %				
Oleic	30	10	—	—
Linoleic	56		—	—
Linolenic	10	—	—	—
C_{20} unsaturated	—	90	—	—
C_{22} unsaturated	—	—	—	—
Saturated	4	—	—	—

[a] *Neo Fat New Fatty Acids and Oils for Industrial Purposes* Armour and Co 1943

and their uses are discussed by Stingley[102] They are suitable for virtually all purposes for which drying oils are used Neo Fat No 190 triglyceride is particularly recommended for admixture with dehydrated castor oil as a substitute for tung oil in the manufacture of spar varnishes and other water resistant and quick-drying finishes Used alone, it produces unduly hard and brittle films This oil, which has an iodine value of about 205, is more highly unsaturated than any natural drying oil

[101] *Neo Fat New Fatty Acids and Oils for Industrial Purposes* Armour and Co , 1943

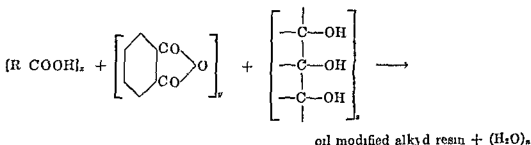
[102] D V Stingley, *Ind Eng Chem* , **32**, 1217–1220 (1940)

(f) Fatty Acid Esters of Substances Other Than Glycerol

A further method of improving the drying properties of oils involves modification of the alcoholic portion of the oil molecule rather than the fatty acids

The esterification of drying oil fatty acids with any polyhydric alcohol containing more hydroxyl groups than glycerol will produce a composition with drying properties superior to those of the corresponding triglycerides (see previous discussion of functionality, page 381) The polyhydric alcohol which may be considered the most probable substitute for glycerol, in case such products attain commercial importance, is pentaerythritol, although the use of other alcohols such as sorbitol, has also been suggested Tests of products of this class have been reported by Long and Chataway,[58] and by Drinberg and Blagonravova [76]

The oil modified alkyd resins may be considered as belonging to the class of substances described under the above heading In the manufacture of these products, the fatty acids from a drying oil are reacted with glycerol and phthalic anhydride or other polybasic acid or acid anhydride, to form a fatty acid–polybasic acid–glycerol complex·



oil modified alkyd resin + $(H_2O)_n$

In some cases the reaction is not carried out directly with the fatty acids, but the oil is rendered reactive by conversion to mono and diglycerides,[103] and these are reacted with the glycerol phthalate or other ester

Glycerol and phthalic anhydride alone readily interact to form linear polymers at moderately elevated temperatures, and at a higher temperature the reaction product is converted into a brittle, insoluble and infusible three-dimensional polymer The incorporation of long chain fatty acids into the product has a plasticizing effect, rendering it tougher and less brittle, and soluble in ordinary solvents If the fatty acids are of the drying oil type, the composition becomes "oxygen convertible," rather than "heat convertible," i e it dries by atmospheric oxidation like an ordinary drying oil, but more readily, and with the formation of a more durable and less reactive film

The percentage of oil or fatty acids commonly incorporated in oil modi

[103] K Ott, H Bernard and F Frick (to E I du Pont de Nemours & Co), U S Pat 2 044,747 (1936)

fied alkyd resins varies between 25% and 75%.[104] Since drying takes place very readily in these products, it is not in general necessary to employ tung oil or other fast-drying oils as the modifying oil. Soybean oil is very extensively used in these resins because of its nonyellowing properties; one of the largest outlets for this class of finishes is in the preparation of white enamels for refrigerators and other household appliances.

The alkyd resins are among the most desirable of all finishes, particularly for metal surfaces, being tough, durable and adherent, and highly resistant to heat, water, and alkaline or acid solutions. One of their chief merits is their characteristically good appearance after prolonged service or exposure. They are much less inclined to chalk, fade, or discolor prior to actual film failure than most other finishes.[104]

6. Manufactured Finishes and Coatings

While any detailed description of the many types of protective or decorative coating compositions is quite beyond the limitations of this volume, an attempt will nevertheless be made to indicate very briefly the nature, composition, and uses of the more important types. Discussion will be confined to those products which are designed to be applied in liquid form, and which dry to form solid films, *i. e.*, to paints, varnishes, printing and lithographic inks, etc. Drying oil products such as linoleum, factice, rubber substitutes, etc., which contain oil in a solid polymerized form, will be discussed in a later chapter (page 418) devoted to miscellaneous oil and fat products.

(a) *Paints*

The term "paint" is commonly applied to any pigmented composition which may be applied to solid surfaces to form an adherent film. In the industry, however, the products designated as paints are usually those prepared with a rather slow drying vehicle of relatively low viscosity, such as unbodied linseed oil, or in some cases, glue or casein solution.

Any paintlike product must have a certain degree of body to enable it to form a uniform film which will not sag or run during the drying period. In the case of slow drying products, it is not sufficient for the applied film to be merely viscous—it must have some degree of plasticity to enable it to withstand the long continued stress of its own weight while drying. Quick drying coatings, on the other hand, may not flow to a serious extent during the drying period if they are merely sufficient viscous.

If the vehicle in a coating composition is lacking in body, this property must be obtained by the incorporation of a large proportion of pigments, hence in all paints there is a relatively high ratio of pigments to vehicle

[104] C. S. Ferguson and J. E. Sellers in *Protective and Decorative Coatings*, Vol. I, edited by J. J. Mattiello, Wiley, New York, 1941, pp. 338-359.

Usually the pigments in a paint contribute from about 25% to as much as 50% of the total volume of the pigment-vehicle mixture Often the amount of pigments required to give the product adequate hiding power is in sufficient for proper consistency, and "extender" pigments of low hiding power are added for the sake of the latter property The ratio of pigments to vehicle employed in different paints is governed by the nature of the surface to be painted, as well as the properties desired in the final paint film Owing to their high proportion of pigments, the characteristics of paint films are to a large extent dependent upon the nature of the pigments On the other hand, in the case of enamels, lacquers or other products which are compounded with a quick drying vehicle of high viscosity and relatively little pigment the character of the film is determined largely by the vehicle

High concentrations of pigments produce a characteristically low gloss or sheen in applied films, hence highly pigmented paints are ordinarily "flat," whereas high gloss is associated with enamels, varnishes, and lacquers, which are either unpigmented or lightly pigmented

Ordinary house paints are usually prepared by mixing a pigment with a vehicle consisting predominantly of boiled linseed oil A small proportion of bodied linseed oil, e g, 8–10%, is often incorporated in the vehicle, since the addition of such an oil improves the durability of the film, and assists in "leveling" or the elimination of brush marks The amount of bodied oil which it is practicable to use is limited by the adverse effect of such oil on the brushing properties of the paint Soybean oil and fish oil are used to some extent in house paints, but due to their slow drying properties and the softness of their films, they are almost invariably mixed with a large proportion of linseed oil Heat-treated perilla oil tung oil, oiticica oil and dehydrated castor oil have been used to some extent in house paints, although normally these oils are rather too expensive in comparison with linseed oil to be common ingredients House paints when applied in three coats, are ordinarily thinned with a small proportion of turpentine or mineral spirits before they are applied, to reduce their consistency, the first or priming coat being thinned to the greatest extent, and each successive coat being thinned less than the one preceding it Recently the "two coat" system of house painting[105] has become very popular, and has to a considerable extent replaced the traditional three coat system This system involves the use of special paints which form thick coatings and produce in two applications a film equivalent in thickness to that obtained in three applications by the older method An essential requirement in two coat work is a priming paint vehicle which does not penetrate deeply into the wood, and which consequently may be highly pigmented Re-

[105] F L Browne, *Ind Eng Chem*, 33, 900–910 (1941).

tention of the vehicle by the pigments is favored by the presence of bodied oils or any other component which promotes pigment wetting

Although ordinary house paints are made with a cheaper vehicle than varnishes, enamels, or lacquers, it must not be inferred that they are necessarily inferior in serviceability to the latter products House paints have certain distinctive properties which make them uniquely suitable for their particular use In this connection it must be remembered that wood is a highly porous material, and that the properties required in a wood coating are in some respects quite different from those required in a coating material for metals or other nonporous substances One highly important characteristic of house paints is their slight permeability to water vapor During cold weather there is in a heated house a temperature gradient extending through the walls from the warm, moist air within the house to the cold exterior air If this gradient is not interrupted by the interposition of a cold air space back of the boards to which paint is applied, condensation of water will take place within these boards to such an extent that they may become saturated A completely moisture impermeable coating will cause liquid water to collect at the paint–wood interface, with subsequent detachment of the coating film[106] Enamels or other products containing varnishes or resins are less permeable to water vapor than ordinary oil paint They also more readily become embrittled from exposure to oxygen and ultraviolet irradiation, in exterior applications, and hence are inclined to fail through cracking or checking

Since a house paint is applied but once to a new surface, which may be repainted many times, the ability of a paint to adhere to its own deteriorated films is highly important In this respect, an ordinary linseed oil paint is outstandingly superior to most other coating materials The character of the deteriorated film is likewise important, both from the standpoint of adhesion of the new film and the appearance of the old film during the period of deterioration Good house paints, unlike other coatings, have certain "self cleaning" properties, there is a tendency for the paint film to gradually chalk off, adherent surface dirt being removed during the process of chalking

Finally, since house paints are usually applied by means of the brush, their brushing characteristics are of some importance Paints which contain a high proportion of pigments are more easily brushed out to a uniform film than more viscous but less plastic coating compositions

Certain of the characteristics associated with the relatively expensive varnishes, enamels, etc , are unnecessary or even undesirable in house paints Very fast drying is of no particular advantage in a product used to paint a house, since it does not speed the over all painting job, and the

[106] J W Iliff and R B Davis, *Ind Eng Chem* , **31**, 1407–1412 1446–1450 (1939)

slightly greater dust pick up of a slowly drying surface is inconsequential in a finish lacking a high gloss Even if it were obtainable, a very high gloss would hardly be desirable in a house paint, since such a finish serves to accentuate minor irregularities of the painted surface, and hence is not particularly pleasing except on very smooth and finely finished surfaces

For painting the screens, shutters, and similar small areas of dwellings, and also for painting certain commercial structures, such as store fronts and gasoline stations, there is a demand for brightly colored, glossy paints which will retain their gloss and brightness of color upon exposure to weathering These so called "trim" or "store front" paints are compounded from raw and bodied drying oils with a certain proportion of varnish or resin Oil modified alkyd resins are said to be particularly desirable ingredients of this class of paints

Various varieties of flat, semigloss, and gloss paints are used in interior decoration Semigloss and gloss interior paints contain varnishes or resins No close distinction can be made between semigloss and gloss paints, or gloss paints and enamels However, in the transition from semi gloss paints, to gloss paints, to enamels, there are encountered progressively higher proportions of varnish or resins, and progressively lower proportions of raw oil and pigments Properly speaking, an enamel is a pigmented varnish Gloss paints approach the characteristics of enamels

Industrial paints, for such structures as factory buildings, smokestacks, tanks, and bridges, and for railway equipment, are manufactured in a very wide variety of forms In general, where the function of such paints is largely or entirely protective, the composition of the vehicle does not differ greatly from that employed in house paints Where decorative effects are to be achieved in coating metal surfaces, there is a tendency toward the use of paints of the enamel type, containing bodied oils and resins

The oil or alkyd emulsion paints comprise a type of coating material of quite different nature from any of those described above There have long been on the market a number of water paints, consisting of dry pigments mixed with lime and some variety of dry, water soluble binder When mixed with water in the proper proportions, these yield a product of a paintlike consistency which dries with evaporation of the water to form a more or less adherent and coherent coating In the earlier water paints, vegetable or animal glues were usually employed as the binding agent Later these paints were improved by replacing glue with casein, or in some cases, vegetable protein materials derived from soybeans Water paints were originally designed only for use as interior finishes, and due to their lack of resistance to water and to weathering they continue to be employed almost exclusively for this purpose, in spite of considerable improvements in their durability

The emulsion paints are of very recent origin, although they are already

widely accepted They are marketed in a paste form, and are of quite different composition from the older water paints They consist essentially of a mixture of pigments with an emulsion of drying oils, varnishes, or resins Many of these products, particularly those modified with oils rather than resins, also contain casein, which apparently acts both to assist the binding action of the oil, and also to maintain the latter in a dispersed condition

Films formed by the emulsion paints have to some extent the properties of oleoresinous coatings of the conventional type, and are much superior to those of ordinary water paints in adhesion, durability, and water resistance The emulsion paints so far marketed, like ordinary water paints, produce only flat finishes, since the ratio of binder to pigments is much lower than in ordinary paints or enamels

(b) *Varnishes, Enamels, and Oil Modified Resins*

Varnishes are of two types, oleoresinous varnishes and spirit varnishes The former, which is commercially much the more important, comprises products made by partially polymerizing a drying oil at a high temperature with resins, and thinning the resulting product to a usable consistency with a volatile solvent Spirit varnishes do not contain oils and consist of resins dissolved in a suitable solvent Enamels are pigmented varnishes

The outstanding characteristics of varnishes enamels, etc , and the characteristics which distinguish these products from ordinary oil paints, are their quick-drying properties and the hardness waterproofness and usually high gloss of their films

Due to the great variety of drying oils, natural and synthetic resins, and solvents now available to the industry, varnishes and related products are manufactured in extraordinary variety, and are among the most versatile of coating materials By a suitable choice of raw materials and compounding methods their properties may be varied widely and closely adapted to specific uses They are universally used as protective coatings for wood or metal surfaces which are subject to abrasion, since paints have poor abrasion resistance, regardless of their ability to withstand weathering Articles manufactured in large quantities by assembly line methods are almost invariably coated with finishes of the varnish type, because of the ability of such finishes to dry quickly, and to respond to heat treatment during drying Varnishes or oil modified resins can be made with a resistance to water or dilute alkalies or acids superior to that of any other flexible coating material Consequently they are now used in applications where ceramic or other nonflexible and difficultly applicable coatings were formerly considered essential Their flexibility readily lends them to such uses as coating fabrics Since they can be made highly resistant to both moisture and heat, they are extremely valuable electrical insulating mate-

rails Owing to the speed with which they dry, they are important ingredients in inks for high speed, multicolor printing In addition to their protective qualities, the decorative properties of these coatings are in general superior to those of paints, because of their high gloss and good color retention

Although tung oil or other conjugated acid oils are generally preferred for varnish making, and in fact may be regarded as more or less indispensable for the production of certain types of varnishes, including those with high water and alkali resistance, there is some use in varnishes of practically all the drying oils The introduction of highly reactive synthetic resins has made possible the production of varnishes or varnishlike materials from oils of relatively poor drying properties Thus, for example, soybean oil is extensively used in the manufacture of oil modified alkyd resins

Varnishes are of short or long "oil length," the length being defined as the number of gallons of oil used in the formula per 100 pounds of resin Different varnishes vary greatly in oil length, according to the variety of oil and of resin used in their composition, and their intended uses In general, however, oil length will vary between about 10 and 75 gallons Since the resins in a varnish are responsible for its hardness and rapid drying properties, whereas the oil imparts flexibility and stability toward deterioration by oxidation, the formulation of a varnish for a particular purpose depends to some extent upon properly balancing the properties imparted by the two ingredients The different resins now available differ so widely in their properties, however, that is is hardly possible to make categorical statements relative to the effect of oil length on the character of the product Thus, for example, varnishes made with natural resins are increasingly durable in exterior applications with increasing oil lengths, whereas a reverse relation is said to hold in the case of phenol formaldehyde resin varnishes [107]

While the essential feature of varnish manufacture is a somewhat prolonged heat treatment of the combined oil and resin, to produce a certain degree of reaction and copolymerization of these two ingredients, the exact manner of conducting this treatment varies considerably according to the nature of the resin and the preference of the varnish maker The harder natural resins, such as kauri, congo, etc , are incompatible with oil in their natural state, and must be subjected to partial heat degradation prior to being heated with the oil This preliminary heat treatment, otherwise known as "melting," "cracking," or "running" is conducted at a higher temperature than the oil will withstand, in certain instances it may be as high as 650°F After running, the melted and homogeneous resin is mixed with hot oil, and heating of the mixture is continued at a lower temperature

[107] R J Moore and W R Catlow, in *Protective and Decorative Coatings* Vol I, edited by J J Mattiello Wiley, New York, 1941, pp 311–337

until it has the desired consistency During this heating period the temperature may rise to 550–600°F The batch may then be allowed to cool slowly, with allowance being made for some extra degree of polymerization during cooling, or it may be quickly cooled to a temperature below that of rapid polymerization, or "checked," by the addition of a small proportion of cold oil When the batch has further cooled, it is thinned with some variety of solvent, after which it is aged for some time, clarified by filtration or centrifugation, and packaged Dryers added to the batch are usually incorporated during the cooling period, in the form of soluble linoleates naphthenates, etc The oil used may be either raw or previously bodied The above description applies only to varnish processing in its simplest form In order to obtain special properties in the product, the batch is often heated, chilled back, reheated with the incorporation of additional resin, etc , in a complicated series of processing steps Certain of the softer natural resins and most of the synthetic resins are relatively oil soluble, and require no preliminary heat treatment, but are simply added to the kettle at the beginning of the heating operation

There are a large variety of natural resins used in varnish manufacture ranging in hardness from the highly fossilized types, such as congo, to recent resins such as dammars, which are tapped from living trees Also properly classified with the natural resins is rosin In general, the price and the general desirability of the natural resins varies with their hardness, with the fossil gums being used in the more expensive products, and rosin or rosin derivatives being used in those of the lowest grades However, the characteristics of the oil also influence the quality of the product, and an ester gum[108] tung oil varnish, for example, may be equivalent to a linseed oil varnish made with a more expensive resin

In recent years, a variety of synthetic resins have been made available in oil soluble form, and have provided the means for producing varnishes and resinous coatings with qualities far superior to those obtainable with any of the natural resins Thus, for example, spar varnishes now prepared with the aid of synthetic resins will resist cold water for 72 to 96 hours and boiling water for 7 hours, without whitening, whereas the older types of spar varnish could be expected to have corresponding resistances of but 18 hours and 15 minutes, respectively[107] The use of synthetic resins has effected equally important improvements in the drying properties of varnishes and enamels The first "four hour" varnishes and enamels were prepared by combining tung oil with modified synthetics of the phenol formaldehyde type, and improved products are now available which dry in less than an hour

The superior drying properties of synthetic resin varnishes are due to the high degree of reactivity of the resins, their high resistance to water and

[108] Ester gum is the glycerol ester of rosin

chemical influences is due to the nonreactivity of the resins in the polymerized form Since the drying of films of such varnishes is principally a matter of polymerization and evaporation of thinner, oxidation entering only to a minor extent, the films are relatively nonsusceptible to deterioration through progressive oxidation after drying is completed, and hence are highly durable Use of the synthetic resins is limited, however, by their relatively high cost Among the synthetic resins used as ingredients of varnishes and related coatings are those of the phenol formaldehyde, alkyd, maleic, urea-formaldehyde, coumarone indene, acrylic, vinyl, and poly styrene types Of these, phenol-formaldehyde and alkyd resins are commercially the most important

The chemical reactions occurring in the varnish kettle are somewhat obscure In the case of natural resins, there appears to be some degree of chemical combination of the resins and the oil, to form mixed polymers, although the extent to which such reaction occurs is by no means clear Some of the synthetic resins clearly enter into chemical combination with the oil, and in fact must be modified by such combination before they are compatible with the oil Others, as for example, the courmarone indene resins, blend readily with oil, but do not appear to react with the oil during the cooking operation

(c) Printing Inks

Properly speaking, printing inks are neither protective nor decorative coatings However, they are so similar to paints and varnishes that they are logically placed in the same classification

Because of the dissimilarity of the different printing processes, and the great diversity of surfaces presented by different papers, etc , a very large number of different inks are required to completely fill the needs of the printing trade In the words of Fuhrmann *et al*,[109] "the technique of ink making consists very largely of detail " For each variety of printing press obtain ration, speed of drying, etc Obviously, therefore, the complete technology of inks is highly involved It will be attempted here to merely indicate the different types of inks, and very briefly outline the composition, characteristics, and uses of printing inks in general

Methods of printing are divided into three main classes While inks of quite different characteristics may be employed with presses of a single class, according to the mode of operation of the press, the nature of the surface to be printed, and the kind of printing desired, there are neverthe

[109] O W Fuhrmann, L O Buttler, P F Duffy, F G Schleicher, and J J Mattiello, in *Protective and Decorative Coatings* Vol III, edited by J J Mattiello, Wiley, New York, 1943, pp 611–651

less certain limitations imposed by the fundamental nature of each process. It is in order, therefore, to briefly consider the three printing methods before proceeding to a discussion of printing inks.

In relief printing the ink is caused to adhere to raised surfaces on the printing plate, from which it is transferred by contact to the paper or other material printed. In gravure or intaglio printing, the design to be printed is indented in the printing plate, rather than raised. The plate is first completely covered with ink, which is then cleanly wiped from the raised surfaces, leaving ink only in the depressions. On contact with the plate, the paper is forced slightly into the depressions, bringing the ink with it as it is removed. In planographic printing, the printing plate has a plane surface, and the design is formed by treating the plate chemically so that portions are easily wetted and ink repellent, and other portions are water-repellent and ink receptive. Planographic printing may be conducted in the ordinary manner, or by the offset process. In the latter process, the paper is not placed directly in contact with the plate, but the ink is transferred from the plate to the surface of a rubber "blanket," and from the rubber surface to the paper.

Most typographic printing is done by the relief method, whereas, the principal uses of gravure and planographic (lithographic) printing are for the reproduction of illustrative material.

Some paper stocks, including ordinary newsprint, are so highly absorbent that "drying" of the ink occurs largely by penetration. In printing such paper, the ink does not actually form a film, and the vehicle merely serves as a carrier for the pigment. Most papers, however, are sufficiently sized to be relatively nonabsorbent so that printing is quite similar to painting, *i.e.* it involves the application of a thin film which must dry by oxidation, polymerization, or evaporation. Hence many printing inks may be regarded merely as special varieties of oil paints or varnishes. In printing ink films, such properties as hardness, elasticity, durability, waterproofness, etc. are of minor consequence, or in some cases of no consequence at all. The principal purpose of a printing ink is to transfer the design afforded by the printing plate cleanly and adequately to the paper. Most printed material is produced in quantity, by presses operating at high speed, and in some processes of color printing, successive films of ink are applied one over the other. For this reason, the drying properties of inks are almost always of great importance.

The ingredients used for compounding printing inks are in general the same as those employed in the manufacture of paints and varnishes, with two important exceptions. Raw or unbodied oils are seldom, if ever, incorporated in printing inks, and for printing on very absorbent paper stock, where no drying is required, a cheap mineral oil is generally substituted for the fatty oil.

The foundation of printing ink formulation consists of the so called lithographic varnishes, which actually are heat bodied oils, usually linseed oils, of varying degrees of body or viscosity. Although a common numbering system is used by different manufacturers for designating the different viscosities of varnish, the specific viscosity associated with each number appears to be subject to some variation. Fuhrmann *et al.*[109] list twelve different varnishes, numbered from 00000 to 8, with approximate viscosities ranging from 2.08 poises for No. 00000 to 137.0 poises for No. 5. The Gardner Holdt[79] standards for lithographic varnishes consist of ten tubes numbered from 000 to 8, omitting No. 7, with viscosities ranging from 1.8 poises at 25°C. for No. 000, to 1250 poises for No. 8. Varnishes of each body are made in both amber and pale grades, the latter being used as vehicles for the lighter, more brilliantly colored pigments. In the formulation of a printing ink, a single varnish is not generally used alone, but varnishes of different bodies are mixed together, to develop to an optimum degree the properties of fluidity, tack, etc.

Other ingredients of printing inks include blown oils, "burnt" oils, mineral oils, dryers, organic solvents or thinners, natural and artificial resins, pigments, and "compounds." Blown oils are principally used in the manufacture of very heavy bodied lithographic varnishes. "Burnt" oils are heat bodied oils which have been prepared by heating the kettle of oil to a temperature above its fire point, then setting fire to its surface and permitting it to burn slowly for several hours. In this manner a product is obtained which is considered to be less "greasy" than ordinary heat bodied oil. Mineral oils are chiefly used as vehicles for newsprint inks, but may also be incorporated as plasticizers in other vehicles. The pigments employed in the greatest volume in printing inks are somewhat different from those which are most popular with paint manufacturers and consist principally of carbon and various synthetic organic materials. Most of the resin used in the manufacture of oleoresinous varnishes for printing inks consists of rosin or ester gum, although many of the synthetic resins also find use in these materials. "Compounds" are waxy materials such as soap, tallow, vegetable waxes, etc. introduced in minor amounts in printing inks to modify the tackiness of the product.

In the following paragraphs the principal types of printing inks are briefly described.

News inks, as mentioned previously, contain no fatty oils, but are prepared with a mineral oil vehicle. However, all other inks, with the exception of a few varieties of the lacquer or spirit varnish type, employ drying oils in their composition. *Cylinder press inks* are relatively slow drying, thin bodied products which dry to a considerable extent by penetration, like news inks. Their vehicles consist of a composite of thin and

medium bodied lithographic varnishes. Cylinder press inks formulated for multicolor process printing must be carefully adjusted with respect to tack and drying properties, in order to permit satisfactory overprinting of the various colors. In a series of such inks the consistencies of the various members of the series must be correlated, each of the successive colors must have less tack than the preceding color, in order that rupture of the ink film will occur in the top layer,[110] or so that each color will be "trapped" by the preceding color. These properties are adjusted by the proper blending of light-, medium-, and heavy bodied lithographic varnishes, and suitable inclusion of dryers and compounds. Some of these inks must necessarily dry quite rapidly, and some are considerably heavier in body than ordinary cylinder press inks. *Job printing inks* are compounded from medium- and heavy bodied lithographic varnishes, and often contain an oleoresinous varnish. They are used for miscellaneous printing on sized, relatively nonabsorbent paper, and hence dry to a large extent by oxidation and polymerization. *Bond inks* are still heavier than job printing inks, and are made with a vehicle consisting of medium and heavy bodied lithographic varnishes and oleoresinous varnishes. They are used for the printing of letterheads, etc., on high grade bond paper, and dry largely by oxidation and polymerization. *Bookbinders' inks* are very heavy, almost to the point of pastiness. They are prepared with heavy oils and varnishes, and are used for printing the covers of cloth-bound books. All of the preceding inks are used in printing by the relief method.

The inks used in connection with gravure or intaglio printing processes are of three principal types. *Plate inks* contain a vehicle consisting of a "burnt" plate oil, mixed with oleoresinous varnishes. They are used for very fine printing, as of bonds, certificates, currency, etc. *Embossing inks* are in effect fast-drying pigmented oleoresinous varnishes. They are used for printing the more expensive stationery, business cards, etc., to produce a characteristic raised design of high gloss and hardness. *Rotogravure inks* are compounded from lithographic and oleoresinous varnishes, with sufficient thinner to produce a very fluid, fast-drying product.

Lithographic inks are products of relatively viscous body compounded from various lithographic varnishes, and in some cases oleoresinous varnishes. The intricate nature of the lithographic process makes the formulation of this type of ink particularly exacting. In addition to very definite requirements in the way of fluidity, adhesiveness, cohesiveness, it is essential that lithographic inks have a minimum tendency to emulsify with the aqueous dampening solutions used to make portions of the plate water-repellent.

[110] H. Green, *Ind. Eng. Chem., Anal. Ed.*, **13**, 632–639 (1941).

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News inks, as mentioned previously, contain no fatty oils, but are prepared with a mineral oil vehicle However, all other inks, with the exception of a few varieties of the lacquer or spirit varnish type, employ drying oils in their composition *Cylinder press inks* are relatively slow-drying, thin bodied products which dry to a considerable extent by penetration, like news inks Their vehicles consist of a composite of thin and

medium bodied lithographic varnishes Cylinder press inks formulated for multicolor process printing must be carefully adjusted with respect to tack and drying properties, in order to permit satisfactory overprinting of the various colors In a series of such inks the consistencies of the various members of the series must be correlated, each of the successive colors must have less tack than the preceding color, in order that rupture of the ink film will occur in the top layer,[110] or so that each color will be "trapped" by the preceding color These properties are adjusted by the proper blending of light , medium , and heavy bodied lithographic varnishes, and suitable inclusion of dryers and compounds Some of these inks must necessarily dry quite rapidly, and some are considerably heavier in body than ordinary cylinder press inks *Job printing inks* are compounded from medium and heavy bodied lithographic varnishes, and often contain an oleoresinous varnish They are used for miscellaneous printing on sized, relatively nonabsorbent paper, and hence dry to a large extent by oxidation and polymerization *Bond inks* are still heavier than job printing inks, and are made with a vehicle consisting of medium and heavy bodied litho graphic varnishes and oleoresinous varnishes They are used for the printing of letterheads, etc , on high grade bond paper, and dry largely by oxidation and polymerization *Bookbinders' inks* are very heavy, almost to the point of pastiness They are prepared with heavy oils and varnishes, and are used for printing the covers of cloth bound books All of the preceding inks are used in printing by the relief method

The inks used in connection with gravure or intaglio printing processes are of three principal types *Plate inks* contain a vehicle consisting of a "burnt" plate oil, mixed with oleoresinous varnishes They are used for very fine printing as of bonds, certificates, currency, etc *Embossing inks* are in effect fast-drying pigmented oleoresinous varnishes They are used for printing the more expensive stationery, business cards, etc , to produce a characteristic raised design of high gloss and hardness *Rotogravure inks* are compounded from lithographic and oleoresinous varnishes, with sufficient thinner to produce a very fluid, fast-drying product

Lithographic inks are products of relatively viscous body compounded from various lithographic varnishes, and in some cases oleoresinous varnishes The intricate nature of the lithographic process makes the formulation of this type of ink particularly exacting In addition to very definite requirements in the way of fluidity, adhesiveness, cohesiveness, it is essential that lithographic inks have a minimum tendency to emulsify with the aqueous dampening solutions used to make portions of the plate water repellent

[110] H Green, *Ind Eng Chem* , *Anal Ed* , **13**, 632–639 (1941)

7. Relation of the Vehicle to Various Properties in Paints and Related Products

(a) *Properties Related to Keeping Quality in the Package*

The ability to withstand long periods of storage in the package is a prime requisite in paint products, since months or even years may elapse between manufacture and use of these materials

Since all paint pigments are heavier than the vehicles in which they are suspended, there is some tendency of pigments to settle to the bottom of the stored cans Under some conditions they may settle out in the form of a hard cake, which will be difficult to mix back into the vehicle Such a caking tendency is of course highly undesirable

The causes and control of settling and caking in paints have been discussed by Croll,[111] Werthan, Wien, and Fatzinger,[112] Gamble,[113] McMillen and Glaser,[114] and others Theoretically, settling can be minimized by decreasing the effective particle size of the pigment or increasing the viscosity or plasticity of the pigment–vehicle system, so that the gravitational force inclining the pigments to settle will be small relative to the resistance to settling offered by the vehicle Actually, however, attempts to control settling in this manner are not always successful, since they tend to merely slow the settling process, without necessarily having any effect upon the condition finally attained by the product after long storage This is particularly true if a high degree of pigment dispersion is depended upon to inhibit settling Highly dispersed pigments settle slowly, but are inclined to form hard cakes if allowed to settle for a sufficient time

Another means of combating the undesirable effects of settling is through control of the character of the settled pigment structure Settling is not necessarily troublesome *per se*, but is undesirable because of its relation to hard caking If the settled pigments form a soft cake, which is readily reincorporated with the oil, the readiness with which the cake is formed may be more or less immaterial The consistency of settled paint pigments is closely related to their degree of flocculation If the pigment particles are highly wetted by the vehicle, or in other words, if they have a high affinity for the vehicle and a correspondingly low affinity for one another, they will tend to settle as discrete particles, with close packing and the formation of a hard cake On the other hand, if they have a relatively low affinity for the vehicle and a strong mutual affinity, so that they tend to clump together in irregular masses, the settled pigment structure will be skeletal, enclosing much of the liquid phase, and soft in consistency

[111] P R Croll, *Ind Eng Chem*, **20**, 734–735 (1928)
[112] S Werthan, R H Wien, and E A Fatzinger, *Ind Eng Chem*, **25**, 1288-1292 (1933)
[113] D L Gamble, *Ind Eng Chem*, **28**, 1204–1210 (1936)
[114] E L McMillen and D W Glaser, *J Applied Phys*, **9**, 502–507 (1938)

Pigment wetting and flocculation may be controlled to some degree by suitable choice of the oils used in the vehicle. Thus, heat-bodied oils wet pigments more readily than raw oils, and the degree of wetting tends to increase with the viscosity of the oil. Blown oils have even stronger pigment wetting properties than bodied oils.

Since flocculation and dispersion in paint products are surface phenomena, it is to be expected that they may be influenced by the presence in the vehicle of small concentrations of substances possessing surface-activity. The substances most commonly added to paints to inhibit hard settling are water (usually to the amount of less than 1%, in the form of a weak soap solution), and metallic soaps, such as aluminum stearate. It is to some extent uncertain how much of the action of these materials is due to surface activity, or modification of the wetting characteristics of the vehicle, and how much is due to the formation of a gel structure in the vehicle. In the case of the metallic soaps, gel formation may be the predominant factor, but water is effective in smaller quantities than are required for strengthening of the vehicle structure through emulsion, hence it probably functions primarily as a flocculating agent.

The defect in paint products known as afterthickening, or if very pronounced, as "livering," involves a thickening of the material in the package. Livering is the result of gel formation in the vehicle, and hence is not related to pigment dispersion, although it is influenced by the chemical nature of the pigment. It occurs most pronouncedly in products made with vehicles of high acidity and reactive pigments. It appears probable that it results largely from gel formation by metallic soaps. However, it has been suggested that highly polymerized oils may be involved in the process,[115] and that gelling occurs after the acidic components of the vehicle have become neutralized, and no longer able to exert a peptizing action.

Livering may be controlled by avoiding the use of highly acid oils, especially with pigments such as zinc oxide, which readily form soaps with free fatty acids. In the case of bodied oils, the method of bodying has a pronounced influence upon livering tendencies.[84] Oils bodied under vacuum form products with less tendency to liver than ordinary oils bodied with access to the air.

Granulation in a paint is usually the result of the deposition of small masses of metallic soaps from the vehicle, and is inclined to occur only with the combination of high acid oils and reactive pigments. Quick-drying varnishes or other products which are inclined to gel with limited oxidation will occasionally form a polymerized film over the surface of the can. This

[115] Chicago Paint & Varnish Production Club, *Natl Paint Varnish Lacquer Assoc Circ* No 471, 289 294 (1934), *Am Paint J*, 18, No 53D, 14–16, *Paint Oil Chem Rev*, 96, No 22, 58–62 (1934)

defect is known as "skinning" It may be inhibited by the addition of "antiskinning" agents [116]

(b) Properties Related to Application of the Films

Paints, varnishes and enamels are applied by brushing, spraying, or dipping, as may be the easiest and most convenient method The manufacture of products which are thin enough to be readily applied by one of these methods, and yet which have sufficient body to "stay put" and form a uniform coating is not always easy, and requires that careful consideration be given to the physical structure of the material

A protective or decorative coating applied to an inclined surface must not flow to an appreciable extent during the drying period if it is to form a uniform film of good appearance and maximum protective properties Films of varnishes or fast drying enamels may have sufficient viscosity to retain their form during the brief period elapsing between application and the beginnings of gelation In the case of paints and other slowly drying products, a certain degree of plasticity is essential to prevent "running" or "sagging" of the films On the other hand, it is not desirable for a paint to be completely resistant to flow after application, particularly if it is to be applied by brushing The ability of the paint to flow slightly permits "leveling," or the elimination of brush marks or other film irregularities by surface tension forces

The manner in which the pigment is dispersed in the vehicle is of extreme importance in determining the body characteristics of the paint Highly flocculated pigment–oil systems tend to be stiff and plastic, whereas dispersed systems are thin and lacking in plasticity As mentioned previously, flocculation may be greatly influenced by the presence of surface active substances developed in the oil by heat bodying or blowing, by the reaction of basic pigments with free fatty acids to form soaps, or by the addition of water, metallic stearates, etc The effect of surface active substances in producing deflocculation and consequent loss of plasticity in a pigment–oil system is dramatically illustrated in the experiment cited by Green,[117] wherein the addition of one or two drops of heat bodied poppyseed oil suffices to convert a stiff mixture of zinc oxide and mineral oil to a fluid mass Recently Fischer and Jerome[118] have published the results of a large number of experiments involving the use of synthetic wetting agents to increase or decrease the flocculation of pigments in various vehicles It is to be noted that the degree of flocculation or dispersion to be attained in a specific system is determined by the characteristics of the pigment as well as the vehicle, and that different pigments respond differently to surface active agents, according to whether they are natu

[116] *Natl Paint, Varnish and Lacquer Assoc Circ* No 400, (1932)
[117] H Green, *Ind Eng Chem*, 15, 122–126 (1923)
[118] E K Fischer and C W Jerome, *Ind Eng Chem*, 35, 336–343 (1943)

rally hydrophilic or lipophilic Thus, for example, ultramarine is considered a hydrophilic pigment, whereas carbon black is lipophilic [118] The former is consequently relatively responsive to deflocculating agents, whereas the latter responds more easily to flocculating agents For photomicrographs illustrating typical flocculated and dispersed pigment–oil systems the reader is referred to such publications as those of Green,[117] Fischer and Jerome,[118] and Troutman [119]

The plastic behavior of paints, printing inks, etc is much influenced by the tendency of these products to behave thixotropically Thixotropy is exhibited by all pigmented paint products,[119a 120 121] and even to some extent by oils alone [121a] Speaking from the standpoint of the practical paint technologist, thixotropy may be defined as the tendency of viscous or plastic materials to become less viscous or to exhibit lower yield values after being stirred, brushed, or otherwise subjected to internal shear It is a reversible phenomenon, the material regains its original viscosity or plasticity when allowed to again remain undisturbed for some time Thixotropy may be so pronounced as to be evident to casual observation It can be detected and evaluated in the laboratory by the technique described by Green and co-workers,[120 121] which involves successive measurements of apparent viscosity at increasing and decreasing rates of shear with a viscometer of the rotational type

Sometimes the term "false body" is applied to the consistency possessed by paints with marked thixotropic properties According to Gamble,[113] false body cannot be clearly differentiated from thixotropic body, but refers in general to body which is quickly regained after disturbance of the material ceases The recovery of thixotropic body is relatively slow In the older literature, the term "false body" is often used with a somewhat different meaning Thus, for example, Werthan *et al* [112] refer to false body as the type of body which may be irreversibly lost as a result of working of the material, as for example, through the breakdown of an emulsion

Thixotropy in some paints may be due in part to the existence of a certain degree of gel structure, but is also undoubtedly associated with the phenomenon of flocculation In other words, a paint which has had its consistency reduced by stirring, brushing, etc , may be considered temporarily deflocculated, the recovery of body after agitation has ceased being coincident with the re establishment of flocculative forces between the pigment particles The thixotropic characteristics of paints and

[119] R E Troutman, in *Protective and Decorative Coatings* Vol III, edited by J J Mattiello, Wiley, New York, 1943, pp 333–385

[119a] J Pryce Jones *J Oil Colour Chem Assoc* 17, 305–375 (1934), 19, 293–337 (1936)

[120] H Green, *Ind Eng Chem*, *Anal Ed*, 14, 576–585 (1942)

[121] H Green and R N Weltmann, *Ind Eng Chem*, *Anal Ed*, 15, 201–206 (1943)

[121a] R N Weltmann, *Ind Eng Chem Anal Ed*, 15, 424–429 (1943)

related materials may therefore be modified by the methods described above for inducing or inhibiting flocculation Kewish and Wilcock[122] have observed a minimum pigment concentration for the appearance of marked thixotropy, which is in the neighborhood of 30% of pigments by volume in the system

In general, some degree of thixotropy is desirable in paints Thus a brushing paint with optimum thixotropic characteristics may thin under the influence of the brush, so as to spread readily, retain its thin consistency long enough for good leveling to take place, and then recover its original thick consistency in time to prevent running or sagging[123] Thixotropy is a particularly useful property in printing inks These materials are applied in very thin films, and hence must be pigmented as intensely as possible A thixotropic ink, which thins markedly during application, may contain a larger proportion of pigment without being excessively thick, than a nonthixotropic product

The degree to which the pigments are wetted by the vehicle has a large influence on the tendency of the vehicle in priming paints to be absorbed by wood surfaces If the pigments and the vehicle have a high mutual affinity, the vehicle will be relatively little inclined to be drawn out of the undried film into the wood Deep penetration of the wood by the vehicle was formerly considered desirable, but it is now known that such penetration is merely wasteful[105] Vehicle penetration must be inhibited by the use of strongly wetting oils, etc, in the primers used for two coat house painting, in order to permit the application of a thick priming coat

Since the factors of pigment settling, ease of spreading, leveling, running, penetration, etc, are all closely related to the matter of pigment flocculation, it will be seen that in general it is not possible to modify the vehicle for the purpose of influencing one of these factors without some effect upon each of the others The very high development of one desirable characteristic may preclude the proper development of other characteristics of equal desirability and importance, or may have an unfavorable effect on the chemical properties of the product The practical formulation of paint materials of good physical characteristics, therefore, involves a series of compromises between mutually exclusive properties, in order to obtain products with the best all around characteristics for the purpose for which they are intended A schematic representation of the qualitative relationships obtaining among the various factors discussed above, is presented in Table 130

The method by which printing inks are applied is fundamentally different from the methods employed for the application of paints, varnishes, etc This difference introduces certain requirements in the way of consistency

[122] R W Kewish and D F Wilcock, *Ind Eng Chem*, 31, 76–83 (1939)
[123] E L McMillen, *Ind Eng Chem* 23, 676–679 (1931)

in these materials Inks are applied by bringing the ink coated printing plate in contact with the paper or other material, to cause the ink to adhere to the latter surface, and then separating the surfaces of plate and paper Unless the paper is so absorbent as to practically remove all ink from the plate, there is in the process of separation a rupture of the ink film somewhere between the two solid surfaces The resistance offered by the ink to this rupture is referred to as its tack

As indicated previously, the tack of printing inks is of great importance, particularly in the case of process inks for color printing, since the successful

TABLE 130

RELATION OF PIGMENT VEHICLE REACTIVITY TO VARIOUS PHYSICAL PROPERTIES OF PAINTS AND RELATED PRODUCTS

A Physical reaction between pigments and vehicle	
Wetting of pigments by vehicle	Nonwetting of pigments by vehicle
Dispersion of pigments	Flocculation of pigments
Thin body	Thick body
Hard caking	Soft caking
Nonthixotropic	Thixotropic
Hard spreading	Easy spreading
Good leveling	Poor leveling
Sagging	Nonsagging
Limited penetration on wood surfaces	Deep penetration on wood surfaces
Lipophilic pigments	Hydrophilic pigments
Bodied oils—blown oils	Raw oils—overbodied oils
No water in vehicle	Water in vehicle
Wetting agent in vehicle	Nonwetting agent in vehicle
B Chemical reaction between pigments and vehicle	
Nonreactivity between pigment and vehicle	Reactivity between pigment and vehicle
No gel structure in vehicle	Gel structure in vehicle
Thin body	Thick body
Nonthixotropic	Thixotropic
Settling	Nonsettling
Good leveling	Poor leveling
Hard spreading	Easy spreading
Sagging	Nonsagging
Not inclined to liver	Inclined to liver
Nonreactive pigments	Reactive pigments
Low acidity in vehicle	High acidity in vehicle (Added metallic soaps)

application of successive colors requires that each color be more tacky than the color applied over it, in order that film rupture may occur in the top, rather than in the bottom film Green[110] has reported the relative tacks of a variety of printing inks, as measured by a specially designed "tackmeter," and has discussed the theory of this property in some detail

The speed with which a paint dries often has an important bearing upon its ease of application The drying time requirements for different products vary a great deal House paints and other exterior finishes are generally considered satisfactory if they will dry reasonably well overnight, under ordinary atmospheric conditions At an opposite extreme are products

used in connection with assembly line production, such as automotive finishes, which, under the accelerative influence of heat, are in most cases dried in much less than an hour

As mentioned previously, the drying rate of an oil is determined primarily by the number and type of its unsaturated linkages In the case of oils containing no conjugated double bonds, the drying rate of the oil is in general shorter the higher the iodine value However, the type of glycerides in the oil, as well as their over all degree of unsaturation, have some influence on the drying rate Fish oils, for example, are generally more highly unsaturated than linseed oil, but they have a high content of completely saturated fatty acids, and hence are relatively slow in forming hard films Conjugated acid oils dry much more rapidly than equally unsaturated oils which do not contain conjugated double bonds

Since drying is to a large extent a phenomenon of oxidation, the drying time of an oil is shortened by the presence of pro oxidants, and lengthened by the presence of antioxidants The metallic dryers commonly used in paints and varnishes serve as pro oxidants The natural antioxidants of drying oils are oxidized and destroyed during the operations of blowing or heat bodying

The drying time of an oil may be greatly shortened by partially polymerizing (heat bodying or blowing) it before it is applied and by incorporating with it resins which are more reactive with respect to polymerization than is the oil These methods of shortening the drying time are employed in the manufacture of varnishes and quick drying enamels

(c) Properties Related to Appearance of the Applied Films

In most applications, paints and other coating materials are required to fulfill a decorative as well as a protective role, hence the appearance of the applied films is a matter of considerable consequence While the color, hiding power, gloss, color retention, etc of such products are largely determined by the characteristics or proportions of the pigments, these properties are also affected to some extent by the vehicle

The hiding power of a paint, or the ability of the paint to obscure the surface over which it is applied, is principally a function of the pigments used However, Lightbody and Dawson[124] have reported that differences of up to 20% in the hiding power of enamels can be produced by the use of different vehicles of the same color and refractive index In the absence of a better explanation, they attributed these differences to variable deflocculation of the pigments, although there was no experimental evidence of this Dark colored vehicles tend to increase hiding power, as compared with light colored vehicles [125]

[124] A Lightbody and D H Dawson, *Ind Eng Chem*, 34, 1452 1456 (1942)

[125] R A Morrison *Official Digest Federation Paint & Varnish Production Clubs*, 4, No 112, 745-749 (1932)

The color of the lighter paints and enamels is considerably affected by the color of the vehicle, only light colored oils are used in the manufacture of enamels of light, bright shades Color retention is very decidedly influenced by the nature of the vehicle Yellowing of white paints and enamels is dependent upon the unsaturation of the oil (see previous discussion of deterioration in paint films, page 380), being little evident in soybean oil, dehydrated castor oil, or other oils containing inconsiderable amounts of fatty acids with more than two double bonds Colored paints of the gloss or semigloss types retain their color and appearance much better when the vehicle is fortified with resins or varnishes A slight chalking tendency, which may be beneficial in the case of a flat white paint because of its self cleaning action, is very detrimental to the appearance of a brightly colored, glossy finish, and may render the latter inadequate from the decorative standpoint long before deterioration has progressed to the point of failure in protection

Gloss in a paint or enamel film is principally determined by the ratio of vehicle to pigments and the fineness of the pigments, but it may also be affected by the presence of certain substances in the vehicle The presence of small amounts of water and of metallic soaps, such as aluminum, zinc, or calcium stearates, is unfavorable to the production of high gloss The effect of these substances on gloss restricts their use as bodying or flocculating agents in some products In certain cases the metallic soaps may be added specifically for their flatting action

(d) *Properties Related to Serviceability of the Applied Films*

Failures of protective coating films may be divided into three categories (a) failure of the film by simple wear or erosion, (b) failure in the structure of the film, resulting in cracking, checking, chalking, etc , and (c) failure of the film to adhere, which may or may not be preceded or accompanied by structural failure

Film failure due to wear or abrasion is chiefly confined to interior finishes, and others which must be periodically washed or cleaned Such finishes are generally of the varnish or enamel type The determining factor in the durability of a film under abrasive conditions appears to be its hardness, which is in turn related to the type of resin employed in the vehicle Varnishes and enamels employing the synthetic resins in their composition are outstanding in abrasion resistance In general, the more highly unsaturated is a drying oil, the harder are its films Pigment flocculation in a paint or enamel is considered detrimental to the hardness of the film In exterior architectural finishes, film failure through simple wearing away of the film is rare, although a similar effect is produced by pronounced chalking

The most common type of film failure is structural, and occurs through gradual alteration of the physical properties of the film as a result of oxida-

tion and continued polymerization The prime cause of this type of failure appears to be a loss of elasticity or of toughness in the film, resulting in eventual cracking or checking, through inability of the film to accommodate itself to externally or internally generated stresses The relation between loss of elasticity and film failure has been the subject of investigations by Hunt and Lansing,[126] and Blom and Krumbhaar [127]

Extreme hardness and resistance to abrasion in a protective coating may be considered more or less incompatible with the elasticity and resistance to embrittlement which is required for long life under exposure to sunlight and other weathering influences Varnishes and enamels are much more inclined to crack or check with age than ordinary oil paints, and their resistance to this type of failure is in general in direct proportion to their oil length and the elasticity of the films However, there are important exceptions to this generalization among products made with some of the synthetic resins Tendency toward the type of failure known as "chalking," if not excessive is considered desirable in white house paints Chalking is a surface type of disintegration, in which the surface of the paint film becomes powdery and gradually erodes away, without the development of structural faults deep within the film A paint which chalks uniformly presents a continually clean, attractive surface during its lifetime, and after erosion has occurred to the point of exposing the painted surface, it offers the best possible foundation for repainting The chalking tendencies of paints are dependent upon the pigments rather than the vehicle, however, being particularly enhanced by the inclusion of titanium dioxide in the formula

Cracking of paint films is often preceded or accompanied by detachment of portions of the film from the underlying surface Loss of adhesion, when accompanied by cracking, may be considered a result of the embrittlement *caused by too advanced polymerization or oxidation*, and hence related to the type of deterioration referred to above Under the proper conditions, however, there may be failure of the film through lack of adhesion without pronounced deterioration of the film itself Adhesion failure of the latter type may be the result of painting over greasy, rusty, moist, or excessively smooth surfaces More often, however, it is caused by the collection of moisture under the paint film after the latter is applied

In connection with the problem of moisture failure, it is to be noted that all films of paints, varnishes, or enamels are to some degree permeable to moisture This permeability is greatest in ordinary oil paints, is less in coatings of the varnish or enamel type, and is very low in some of the varnishes prepared from the phenolic and other synthetic resins With respect to the function of the coating material, a sharp distinction must

[126] J K Hunt and W D Lansing, *Ind Eng Chem* 27, 26–29 (1935)
[127] A V Blom and W Krumbhaar, *J Oil Colour Chem Assoc*, 21, 338–354 (1938)

be made between metals and other nonporous substances, and wood or similar materials which are permeable to moisture, and a further distinction must be made between wood members which are completely sealed by the coating material, and others which are coated on one side only, such as the sidings of frame dwellings If the material painted is impervious to moisture, or if it is sealed on all sides by the paint, a maximum degree of waterproofness is desirable in the vehicle But if it is sealed on but one side, it may be desirable for the paint film to be capable of transmitting moisture rather freely, as otherwise water may be driven through the wood from the unpainted side, and if it is then unable to escape, it will collect between the paint film and the wood surface, causing the two to become nonadherent

Although ordinary house paints are much more permeable to moisture than varnishes or enamels, they may exhibit moisture failure under adverse conditions This type of failure has become much more prevalent since insulation of the walls of houses has become a common practice If the insulating material is placed directly back of the siding, without an intervening air space, much of the temperature gradient from the inside of the house to the atmosphere will be in the siding, and moisture from the warm air within the building will tend to condense on the unpainted interior siding surface

Metal surfaces are usually painted to avoid rusting, hence the water resistance of metal paints is important However, in general, reliance is placed on a preliminary rust inhibitive treatment, such as the "Bonderizing" process, or the use of rust inhibitive pigments, rather than special vehicle formulations, to minimize rusting on painted metal surfaces Moisture penetration of woods leads to warping and swelling, hence much attention is given to obtaining maximum waterproofness in spar varnishes or other coating materials for nonarchitectural wooden surfaces The conjugated acid oils, and particularly tung oil, are outstandingly superior to ordinary drying oils for the manufacture of highly water resistant varnishes Among the products which are the most desirable in this respect are varnishes compounded from tung oil and the phenolic resins For extreme water resistance, as required for example in interior coatings for tin cans, phenolic resin spirit varnishes, or very short tung oil varnishes of the baking variety are used

CHAPTER XIV

MISCELLANEOUS OIL AND FAT PRODUCTS

In addition to the materials included in the major classes of oil and fat fat products, and described in the preceding chapters, there are a number of others of considerable industrial importance In some cases these consist either wholly or substantially of fats or their derivatives, in others the fat or oil is an essential ingredient

In general, the manufacture of these miscellaneous or specialty products is not standardized to nearly the same degree as that of the more widely used fatty products Often their preparation is more of an art than a science, and the method of manufacture and the materials used vary widely from one manufacturer to another Because of this, and also because of the great diversity of minor uses for fats and oils, it is hardly possible to review this field as comprehensively as those previously covered However, an attempt will be made to indicate the nature and composition of the more important minor products

In a considerable number of minor or specialty uses a fatty oil is employed because of its ability to dry or polymerize In many applications where polymerization does not enter, the fatty oils compete to some extent with mineral oils Since the latter are stable toward oxidation and also relatively cheap, they are generally preferred except where the distinctive properties of the fatty oils or fatty acids confer upon these materials particular advantages

1. Drying Oil Products

(a) *Linoleum*

The essential material for the manufacture of linoleum is a specially prepared, highly oxidized and polymerized drying oil which has been compounded with rosin, and in some cases other natural or artificial resins to yield a stable, resilient, yet thermosetting product known to the industry as "cement" The cement is mixed with ground cork or other similar material, and suitable pigments, and pressed onto a backing of burlap or other coarse fabric In so called inlaid linoleum, the design is made up of separate blocks or other figures of cement, which are pigmented with different colors This method of manufacture causes the design to extend some distance into the linoleum, so that it is not readily worn away Linoleum is flexible and resilient, relatively nonconducting to heat, and

very durable True linoleums are to be distinguished from the much cheaper and less durable felt base floor coverings which contain no polymerized oil, but are made by impregnating a feltlike material with bitumen, and applying on the surface a thin coating of enamel

The first step in the manufacture of linoleum is the oxidation and polymerization of linseed oil or other suitable drying oil or mixture of oils, until a relatively dry, nontacky solid is produced The process is emphatically one of oxidation polymerization rather than heat polymerization, being carried out at a temperature not in excess of about 120°F Polymerization at a higher temperature, *e g*, 140°F or above, is said to yield an inferior product

Originally, polymerized oil for the manufacture of linoleum was made by the "scrim" process, wherein lengths or scrims of light cotton fabrics were suspended in a warm room provided with air circulation and periodically (about every 24 hours) flooded with previously boiled oil After about 3 to 6 months the fabrics became coated with a layer of polymerized oil about 1 inch thick which was then stripped off The scrim process is now largely superseded by the "smacker" process, in which the oil heated to about 120°F is stirred in a horizontal jacketed drum equipped with a horizontal agitator with radial arms or paddles, under a strong current of air Before it is charged to the smacker, the oil may be previously polymerized to some degree by being circulated in a warm atmosphere and allowed to fall continuously in a spray The entire operation will require from about 4 to 6 days In the smacker the oil may be mixed with a small quantity of whiting After the polymerized oil is cooled it is cut up into chunks, which are then stored or "stoved" for several days at about 100°F During this period the product becomes still stiffer and more crumbly, and if whiting or other carbonate is present it will swell, and assume a honeycombed structure, through the generation of carbon dioxide produced by the action of acidic products of oxidation on the carbonate

In the second step in the preparation of linoleum cement, the polymerized oil is fluxed with rosin or other resins The resin mixture originally recommended consisted of equal parts of rosin and kauri gum, but the latter gum is now said to be often omitted [1] Approximately 1 part resin is used to 4 parts polymerized oil The oil and resins are heated together at about 275° to 300°F until the desired degree of reaction and thickening have occurred Actual chemical reaction occurs between the ingredients, to yield what is in effect a particular variety of synthetic thermoplastic resin After the product is cooled, it is cut into slabs and cured for a period of several days before it is worked up

The final step in the development of the body of the finished material

[1] A B Miller and F D Snell, *Ind Eng Chem*, 25, 1307–1311 (1933).

takes place after the linoleum is formed, when it must be again cured by "stoving" at a moderately elevated temperature for a period of several days or weeks

Linoleum cement is not merely another form of infusible drying oil–resin polymer, similar to that in an ordinary dried varnish film As pointed out by Miller and Snell,[1] in the manufacture of linoleum the separate processes of heat polymerization and oxidation polymerization are reversed from their usual order, as in the formation of protective coatings It is particularly to be noted that linoleum cement is unlike a hardened paint or varnish film in that it is fusible and thermosetting This property is important in its relation to the mechanism of linoleum manufacture Fusibility in the cement is particularly essential in the manufacture of inlaid linoleum, as this process requires the welding together of many separate blocks of material, and the reworking of much scrap

TABLE 131

OILS USED IN THE MANUFACTURE OF LINOLEUM AND OILCLOTH IN THE U S IN 1941[a]

Oil	Million lbs
Soybean oil	7 7
Linseed oil	110 2
Tung oil	1 9
Perilla oil	0 3
Castor oil	1 3
Other vegetable oils	0 7
Fish oils	14 7
TOTAL	136 8

[a] U S Bur Census, *Animal and Vegetable Oils*, 1938–1942 Washington, 1943

The chemistry of linoleum cement manufacture is even less well understood than that of ordinary polymerization processes involving a drying oil The reaction occurring between the polymerized oil and the resin in the fluxing operation undoubtedly involves condensations, esterification, and intermolecular rearrangements The monofunctional character of the rosin is considered important[1], presumably it modifies the polymerization of the polyfunctional glycerides, to preserve the heat-convertible nature of the product The chemical aspects of linoleum making are discussed at length by de Waele [2] The theories of this author, while now old, do not appear to have been greatly improved upon

The consumption of the various oils in linoleum and oilcloth manufacture in the United States in 1941 is shown in Table 131

In the manufacture of linoleum, as in the manufacture of varnishes, the development of synthetic resins has greatly extended the variety of available raw materials The coumarone indene resins are said to be particularly suitable substitutes for kauri gum in linoleum cement

[2] A de Waele, *J Ind Eng Chem*, 9, 6–18 (1917)

(b) *Oiled Fabrics*

There are two classes of oiled fabrics, consisting of those exemplified by ordinary "oilcloth," in which the oil forms a continuous coating on one side of the fabric, and those in which the entire fabric is impregnated with oil Fabrics of the first class are used as coatings for walls, tables, shelves, and other surfaces which are not walked upon, or otherwise are not subjected to sufficiently severe abrasion to require a linoleum coating Those of the second class are coated to make them water repellent, and are chiefly used for raincoats, machine and instrument covers, etc Both classes, but particularly the second class, must be pliable

Oilcloth is made by applying successive coats of paints and varnishes to a cotton backing, with the final coat being designed to impart to the surface a high gloss The paints and varnish must be compounded to produce a coating which will withstand moderate flexing without cracking, hence they cannot be made exclusively with highly drying oils, but must contain plasticizers

Linens and silks are the fabrics which are usually oiled The oiling operation consists merely of thoroughly impregnating the fabric with unpigmented drying oils, and allowing each application of the oils to thoroughly dry Strongly drying oils such as perilla or tung oils are less suitable for this purpose than oils which yield softer and more pliable films, such as linseed and fish oils

The cordage used in fishing nets, etc , is usually oiled, the oils most used for the purpose consisting of linseed oil and fish oils

(c) *Putty and Other Sealing Materials*

There are a variety of sealing materials and cements which have a drying oil base, of which ordinary putty is the most common example Putty is usually composed simply of a thick, plastic paste of whiting and linseed oil Some sealing materials with a fatty oil base are treated to produce a rubber like material Others are more nearly like heavy paints or varnishes The stearine pitch remaining from the distillation of fatty acids may be placed in this category of products, it is used in the manufacture of wall board, floor tiling, electrical insulation, industrial paints, and other products requiring a relatively high grade pitchlike material

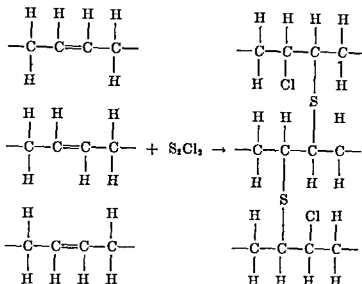
(d) *Rubberlike Materials*

Unsaturated fats and oils, and particularly the drying oils, are capable of polymerizing to form various elastic, rubberlike materials

The oldest materials of this class are the factices, which are polymerized with the aid of sulfur The action of sulfur is in this case entirely similar to its action in the vulcanization of rubber, *i e* , it modifies the structure

of the polymer by providing a ready means of cross bridging through the sulfur molecules

There are two varieties of *factice*: white and brown White factice is prepared by reacting a relatively saturated oil, such as castor or rapeseed oil, with liquid sulfur monochloride The reaction takes place readily in the cold, and may be ideally represented as follows:



Actually, the reaction appears to be quite complex Obviously, simple addition of sulfur and chlorine atoms at the double bonds can take place in a number of different ways, with each molecule of sulfur monochloride eliminating from one to three double bonds, hence there is no particular relation between the unsaturation of the oil and the amount of reagent absorbed [3] Substitution also appears to take place, since in some cases, particularly in the treatment of highly unsaturated fish oils, there is a considerable evolution of hydrogen chloride gas

White factice is a light colored, compressible, but more or less crumbly material, which is principally used as an extender or modifier for rubber An important use for this material is in the manufacture of erasers, wherein it confers that degree of friability which is essential in this product

Brown factice is made by first blowing a drying oil until it is thickened, and then reacting the partially polymerized oil with about 5–30% of its own weight of powdered elemental sulfur The reaction is carried out in a closed vessel, with stirring, at a temperature of about 250–350°F, over a period of 1–2 hours Depending upon the percentage of sulfur, the temperature and the reaction time, the product varies in consistency from a dark, viscous, and sticky semisolid, to a hard and relatively brittle solid The characteristics desired will depend upon the specific use to which the factice is to be put The chemical reactions taking place in the manu

[3] H P Kaufman, J Baltes, and P Mardner, *Fette u Seifen*, 44, 337–340 (1937)

facture of brown factice are undoubtedly even more complex than those involved in making white factice, but again they may be likened to those occurring in the vulcanization of rubber

Brown factice is used not only as a rubber extender, but also to modify the properties of drying oil products, as in varnishes, linoleum, etc

Quite recently another type of drying oil polymer has been developed, which has to a considerable extent the properties of natural rubber This product, developed under the name of Norepol, and also manufactured in the original or a modified form under the trade names of Agripol,[4] Vulprene,[5] etc , is made from soybean or linseed oil The essential step in the manufacture of this material embodies a novel method for the separation of polymerizable from nonpolymerizable fatty acids The polyfunctional glycerides are converted to a monofunctional form by reaction of the oil with methyl alcohol or other monohydric alcohol, to yield monoesters The latter are then heat polymerized, the reactive esters principally forming dimers, and the nonreactive esters remaining as monomers The latter are removed from the mixture by fractional distillation, and the monohydric alcohol attached to the dimeric residue is replaced with ethylene glycol This product is then further polymerized, after which it may be vulcanized and compounded to yield the finished rubberlike material

The products so far manufactured lack the tensile strength and abrasion resistance of natural rubber and some other synthetic products, but are satisfactory for most purposes where these properties are not of prime importance They are particularly suitable materials for gaskets, stoppers, bumpers, tubing, electrical insulation, etc

(e) *Core Oils*

Core oils are used as binding agents for the sand cores of hollow metal castings The cores are prepared by mixing approximately 50 parts by volume of sand with 1 part of oil, molding the mixture in a wooden form, and baking at a temperature of about 400° to 450°F until a hard, coherent mass is formed The sand is usually dampened to make it more easily molded, and a water soluble binder, such as casein, dextrin, etc is sometimes added to assist in maintaining the core in the proper form until it becomes hardened through heat polymerization of the oil

The core should have sufficient mechanical strength to retain its form during the casting operation, but should of course not be so hard as to be difficult to break and remove from the finished casting It must have a certain degree of permeability, to permit the escape of gases evolved during casting Test specimens baked and tested in an ordinary cement tester should have tensile strengths of the order of 200 lbs per sq in

[4] C A Braidwood, *Chem Industries*, **52**, 322 324 (1943)
[5] R T Nazzaro and W Abramowitz, *Rubber Age*, **52**, 483–486 (1943)

The oils used in core making include linseed, soybean, and fish oils The drying properties of the oil are sometimes enhanced by the addition of metallic dryers and rosin

(f) Tanning Oils

In the operation of oil tanning, the skins are impregnated with a suitable drying oil, and stored at a warm temperature (e g, 100°F) until considerable oxidation of the oil has taken place The excess of oil is then removed by scouring Tanning occurs as the result of chemical combination of aldehydes or other products of oxidation with the collagen of the skins In the process a sufficient amount of oil or of long chain glyceride fragments is fixed to make the finished leather very soft and pliable

Oil tanning is employed in the tanning of furs, and also for making chamois and other washable leathers, for gloves, etc

The oils used in tanning consist exclusively of marine oils, of which cod oil appears to be particularly preferred The particular desirability of marine oils is attributed by Dean[6] to the fact that they contain substantial proportions of both highly unsaturated acids and acids relatively lacking in unsaturation Since the fatty acids tend to be evenly distributed in the glyceride molecules, the average molecule will thus contain both highly unsaturated acids, to make it oxidizable and reactive with the leather, and saturated or monoethenoid acids, to remain unoxidized and contribute a lubricating action

2 Lubricants and Plasticizers

(a) Lubricating Oils

Although fatty oils were once extensively used as lubricants for machinery, they are now largely supplanted by mineral oils The latter do not hydrolyze and thus become acid and corrosive in use, and in addition they are cheaper than fatty oils However, fatty oils have certain special advantages, which have insured their continued use in limited quantities The principal virtue of these oils as lubricants results from their superior ability to cling to metal surfaces in the form of very thin films Actually, this property appears to be largely due to the surface activity conferred by the small amount of free fatty acids occurring in the oils[7], the free acids are polar in nature and tend to become adsorbed in layers of molecular dimensions at the metal–oil interface The interposition of such films is

[6] H K Dean *Utilization of Fats* Chemical Pub Co, New York 1938 p 277

[7] For a complete discussion of the function of surface active compounds in lubricants see G L Clark, B H Lincoln and R R Sterrett, *Proc Am Petroleum Inst III*, **16**, 68–80 (1935)

effective in preventing metal seizure under conditions of extreme pressure, or under other conditions tending to displace gross films of lubricant between the bearing surfaces. Fatty oils are also less easily displaced from metal surfaces by water than are mineral oils and hence are valuable ingredients for lubricants designed for the cylinders and valves of steam engines.

Sulfurized fatty oils are sometimes added to lubricants simply for the sake of the sulfur that they carry. This is particularly practiced in the case of cutting oils and extreme pressure lubricants. It is considered that the sulfur prevents contact between closely opposed ferrous metal surfaces through the interposition of a film of iron sulfide.

Fatty oils are used in some quantity for the lubrication of very light machinery and delicate mechanisms, such as watches, clocks, scientific instruments, spindles, looms, sewing machines, etc. The oils which are suitable are those which are sufficiently saturated to be free from gumming tendencies, yet which are liquid at ordinary temperatures. These include lard oil, neatsfoot oil and sperm oil, the latter, of course, being actually a liquid wax rather than an oil. Olive oil belongs to the class of liquid, nongumming oils, but is little used as a lubricant because of its high price.

Castor oil is more viscous than ordinary oils and hence is suitable for lubricating fairly heavy machinery. Its viscosity changes relatively little with temperature, and it has a low cold test or solidifying point (*ca.* 0°F.), hence it was once considered more or less essential for the lubrication of airplane motors. In this and similar applications it has now been replaced to a large extent by the newer low cold test mineral oils.

There is a considerable production of blended oils, comprised of mineral oils containing a fatty oil or fatty acid. "Blown" rapeseed oil, or rapeseed oil which has been thickened by polymerization, is a particularly common ingredient of such products. It not only contributes surface active properties to the blend, but also increases the viscosity of the mineral oil. Blends containing from about 5% to 25% of fatty oil are particularly used for machinery operating under heavy loads, or at high temperatures, such as marine and Diesel engines. The blends are less easily washed away from metal surfaces by water and steam than ordinary mineral oils, and hence are preferred for the lubrication of steam engines.

The well known "germ" process of Southcombe and Wells[8] for the improvement of lubricating oils originally embodied the incorporation of a small proportion, *e. g.*, 0.5%, of a fatty acid. However, certain chlorin

[8] J. E. Southcombe and H. M. Wells, U. S. Pat. 1,319,129 (1919), Brit. Pat. 130,877 (1918).

ated fatty acid derivatives[9, 10] appear to be superior to the simple fatty acids for this purpose.

(b) *Lubricating Greases*

Many mechanical devices are constructed in such a manner that they cannot be conveniently or efficiently lubricated by a liquid oil, but require a semisolid, plastic lubricating grease. These greases consist of lubricating oils stiffened by the addition of various soaps.

Lubricating greases are prepared by heating a mixture of lubricating oil and soap to a high temperature, to form a homogeneous solution, and then cooling the mass with continuous agitation. Soap separates upon cooling in the form of curd fibers, and neat soap or other liquid crystalline material, and being intimately dispersed in the oil, forms with the latter a plastic solid. The characteristics of the finished greases depend upon the mineral oil used, the relative proportions of oil and soap, the fatty materials going to make up the soap, the metal used for forming the soap, the degree to which the soap is hydrated, and the method of solidifying the grease The diverse lubrication requirements of modern machinery make the technology of these products highly involved. It will be impossible to present here more than a bare outline of the subject.[11]

TABLE 132

FACTORY CONSUMPTION OF FATS AND OILS IN THE MANUFACTURE OF LUBRICANTS IN THE U. S DURING THE YEAR BEGINNING JULY 1, 1942[a]

Fat or Oil	Million lbs
Tallow	25 6
Greases[b]	19.0
Rapeseed oil	13 7
Marine animal oil	6.4
Wool grease	4 7
Fish oils	2 0
Soybean oil	1.2
Cottonseed oil	1.1
Linseed oil	1 0
Castor oil	0 8
Other vegetable oils	0 9
Other animal and marine oils	0 1
TOTAL	77 3

[a] U S Bur Census reports.
[b] Including a small amount of lard.

[9] L. L. Davis, B H. Lincoln, and B. E. Sibley, *Proc. Am. Petroleum Inst. III*, **16**, 81–103 (1935).

[10] B. H Lincoln, G. D. Byrkit, and W. L. Steiner, *Ind Eng. Chem.*, **28**, 1191–1197 (1936).

[11] For detailed information on the chemistry and technology of lubricating greases, see the monograph of E. N. Klemgard, *Lubricating Greases Their Manufacture and Use* Reinhold, New York, 1937. For further information on the theory of soap-mineral oil systems, see the references quoted in footnotes 14 and 15, and also A. S. C. Lawrence, *Trans. Faraday Soc.*, **34**, 660–677 (1938); *J. Inst. Petroleum Tech*, **24**, 207–220 (1938).

The fats used in lubricating greases consist principally of inedible tallow and greases, and commercial stearic and oleic acids although there is some use of such materials as palm oil, neatsfoot oil, lard oil, etc The metallic portion of the soap generally consists of sodium calcium, or aluminum Recently lithium stearate greases have attained considerable popularity particularly for use on aircraft Lead soaps are incorporated in certain types of greases, but for their lubricating value, rather than their stiffening effect In addition to mineral oil and soaps, greases may also contain such ingredients as asphalt, petrolatum, mineral wax, rosin, dyeing and perfuming substances, and inorganic materials including graphite, and other nonabrasive solids If a fat rather than a fatty acid is used in forming the soap, and saponification is carried out directly in the mineral oil,[12] as is often the practice, glycerol from the fat will remain in the grease In some cases, particularly in that of calcium soap greases, considerable un reacted fat may remain in the grease, as well as substantial amounts of free alkali A small amount of water is commonly associated with the soap

The consistency of a lubricating grease will depend much more upon the amount of soap incorporated than the viscosity of the mineral oil Often a series of greases of widely varying consistency is prepared from a single mineral oil, by simply using different proportions of soap Thus, for example, ordinary calcium base cup grease may contain from about 7% soap in the No 00 grade to about 35% soap in the No 6 grade This is the ordinary range of soap content in most greases, although considerably less soap may be used where the object is merely to thicken a fluid oil, and very stiff, high melting greases designed for service at high temperatures, such as locomotive driving journal compounds, may contain 50% or even 60% soap

The body characteristics of lubricating greases are naturally related in an intimate way to the crystal or gel structure of the soap phase Farrington and Davis,[13] as a result of microscopic study of greases have proposed a classification of these materials upon the basis of the average length of their soap fibers, as follows

Type	Fiber length microns	Character
Long fiber	100 or more	Fibrous ropy
Medium fiber	10 to 100	Clinging slightly rough
Short fiber	1 to 10	Slightly rough short
Microfiber	Less than 1	Smooth unctuous

[12] W Gallay and I E Puddington, *Can J Research*, **B22**, 76–89 (1944) have described extensive experiments in the preparation of various metallic soaps in mineral oils at relatively low temperatures For general information on saponification in nonaqueous systems see V R Kokatnur, U S Pat 1 813 454 (1931), and J J Jacobs, *Ind Eng Chem* **34**, 322–326 (1942)

[13] B B Farrington and W N Davis, *Ind Eng Chem*, **28**, 414–416 (1936)

The presence of fatty acids, glycerol, or other polar substances in the material during crystallization has a large effect upon the character of the grease, as these substances promote wetting of the soap phase by the mineral oil, and the growth of soap fibers [14] The application of shearing forces (through agitation) during the process of crystallization also facilitates the development of long fibers [15] Since soaps of other metals as well as sodium soaps are polymorphic, *i e*, capable of existing in more than one crystal modification, the character of the solid particles depends to a large extent upon their crystal form, which in turn is determined by the conditions under which solidification is carried out

A recent publication by Houlton[16] emphasizes the degree to which the consistency of aluminum and lithium stearate greases is dependent upon the method of solidification

According to Farrington and Davis,[13] the suitability of greases for specific uses can be correlated with fiber length Thus long fiber greases are particularly adapted to use in gear boxes, since they are readily worked between the moving parts by the action of the gears, and they tend to take up the slack in worn gears and eliminate noise Also they are easily retained within a gear housing On the other hand, greases of this type are not good lubricants for ball and roller bearings, since they do not cling well to the balls and rollers Short fiber greases are the most suitable for locomotive journals and open type roll bearings, whereas cup greases are always of the microfiber type

Long, medium, and short fiber greases are made with sodium soaps, calcium, aluminum and lithium yield microfiber greases Aluminum base greases are particularly fine grained, and have a clear, translucent appearance, which gives them a desirable sales appeal Lead soaps (usually lead oleate) are used in a number of railroad greases including journal box lubricants, and in combination with sulfurized fatty oils are considered more or less essential ingredients of hypoid gear and other extreme pressure lubricants

(c) *Cutting Oils*

Cutting oils are used for the lubrication of tools for the cutting or machining of metals In some cases the oils are used as such, and in others they are employed in the form of an emulsion with water The cutting fluid not only performs a lubricating function, permitting the tool to slide between the cutting and the face of the machined member with a minimum

[14] W Gallay and I E Puddington *Can J Research* **B21**, 202 229 (1943) W Gallay, I E Puddington and J S Tapp *ibid*, **B21**, 230–235 (1943), **B22**, 66–75 (1944)

[15] W Gallay and I E Puddington, *Can J Research* **B22**, 90–108 (1944)

[16] H G Houlton B D Miller P A Lenton J A Taylor and B E Adams *Oil & Soap*, **21**, 258 263 (1944)

of friction, but also cools the tool, and washes away chips and particles of detached metal

The standard cutting oil of the nonemulsifying type was for many years lard oil Ordinary mineral or paraffin oil is quite inadequate as a substitute for lard oil, but satisfactory products containing a minimum quantity of fatty oil are now prepared by compounding a sulfurized fatty oil with mineral oil Oils of this type are principally used for thread cutting and similar applications where a heavy cut is taken at a relatively low speed

For high speed cutting an emulsion type cutting liquid is usually employed The nonaqueous base for a liquid of this type may consist substantially of soap, a sulfonated oil, or a mixture of mineral oil with sulfonated oil or soap

Wire drawing compounds, molding compounds, etc, may logically be classed with the above materials These usually have a soap base, but in addition to soap, talc, graphite, etc, they sometimes also contain fatty oils or mineral oil, and thus have something of the nature of lubricating greases

(d) *Oils for Leather Lubrication*

The fibers of finished leather must be lubricated with a thin coating of oil, to enable them to readily slide over one another as the material is flexed The liquid oils which are most used in leather treatment[17] are neatsfoot oil and fish oils, particularly cod oil Tallows and greases are the plastic fats usually employed There is also some use of waxes, such as wool grease, beeswax, and carnauba wax, as well as paraffin wax and mineral oils

Light leathers are usually oiled by the so called fat liquoring process, wherein the skins are tumbled in a drum containing a dilute emulsion of oil and water stabilized by a sulfonated oil The sulfonated oil serves to carry the oil to the interior of the skins, where it is deposited by subsequent breaking of the emulsion Heavier leathers are oiled by the hand stuffing process, in which the damp leather is smeared with a plastic grease or "dubbin," consisting typically of a mixture of tallow and cod oil The high melting fat in this composition is not absorbed, but serves merely as a vehicle for the liquid oil and is removed at the conclusion of the operation If it is desired to cause the leather to absorb higher melting fats or waxes, it may be "drum stuffed," by tumbling the wet leather in a drum with the melted fat Other methods of incorporating the oil are by "burning in," or applying the hot melted fat by hand to the dry leather, and dipping the leather in the melted fat The latter methods are principally employed where it is desired to impart some degree of waterproofness to the material

[17] For detailed information on the oiling of leather see J R Blockey, *The Application of Oils and Greases to Leather* Shoe and Leather Reporter Co, Boston 1919

In all methods of oiling leathers, the distribution of oil is assisted by the action of water One function of the water appears to me to cause the leather fibers to spread and separate The presence of water also favors the spreading of oil films on the fibers, in some manner as yet but little understood In the methods mentioned above in which oil or fat is applied to the dry leather, the oiled leather is later drummed with warm water, to distribute the fat

The grain surface of wet vegetable tanned leather is "oiled off" by the application of a thin oil coating before the leather is dried, to lubricate the grain, and to permit the leather to dry without the concentration of tanning liquors at the surface Some leathers, e g, sole leather, receive little or no oiling except in this operation

In the lubrication of leathers the chemical reactivity of the fatty oils is important, hence mineral oils are not suitable substitutes The action of leather treating oils is not purely physical, some degree of chemical combination apparently occurs between the leather and the oil since the latter is not readily removed after it is once incorporated, even upon treatment with solvents

(e) *Textile Lubricants*

Textile lubricants are used for rendering textile fibers pliant, and enabling the fibers to move smoothly over one another in the operations of combing spinning weaving, etc Any lubricants applied to the fibers in the course of processing must of course be removed from the finished textiles Fatty oils are much more easily removed than mineral oils, and in addition are superior lubricants, hence are used almost exclusively for this purpose

Sulfonated oils of various types are principally used as lubricants for cotton textiles and the various synthetic fibers, but there is some use of straight oil, usually inedible olive oil, as a worsted lubricant Other liquid oils of a more unsaturated nature are not suitable substitutes, since they are inclined both to gum and to undergo rapid oxidation after application, with generation of heat and consequent hazard of spontaneous combustion

(f) *Plasticizers*

Whenever a fatty material is incorporated into a composition for its plasticizing effect, its function may be considered essentially one of lubrication The fatty materials used as plasticizers consist of both fats and fatty acids Of the former, castor oil is a particularly valuable agent, as its content of hydroxy acids enables it to be incorporated in products with which ordinary fats and oils are incompatible

Fatty plasticizers are used in a very wide variety of materials, including rubber, nitrocellulose, and many synthetic plastics

3 Illuminants

The production of cheap illuminants[18] from petroleum has virtually eliminated fatty oils as burning oils, except in isolated regions where petroleum is not available, but there is still some use of fatty materials in candle manufacture Although the basic materials for candles consist of paraffin wax and beeswax, candles made from these materials alone are not sufficiently high melting to maintain their shape well in hot weather or to burn without excessive dripping Stearic acid has long been the standard hardening agent for candles, and since the advent of the hydrogenation process there has also been considerable use of very highly hydrogenated fats for this purpose, either as such or more usually in the form of their fatty acids

The amount of stearic acid or other fatty hardener used in candles depends upon the type of candle and the other ingredients, it may be as little as 5%, or as much as 50% or more

4. Cosmetic, Pharmaceutical, and Medicinal Oils

In cosmetics as in many other products, petroleum fractions have taken over many of the traditional functions of fatty oils However, oils, fats, and fatty acids are still important materials in the cosmetic and pharmaceutical industry

Fats in the form of almond oil, olive oil, palm oil, hydrogenated lard, etc are used in the treatment type of creams ointments and lotions since they are more readily absorbed by the skin than mineral oils Vanishing creams, foundation creams, powder bases, etc are basically similar to brushless shaving creams, *i e*, they consist of an emulsion with a base of incompletely saponified stearic acid

Castor oil is used in hair dressings because of its property of mixing freely with alcohol It is also used as a plasticizer in nail polishes

Stearic acid in the form of zinc, calcium, and magnesium stearates is much used in face, bath, and talcum powders

Many cosmetic preparations contain fats in the form of soaps, sulfonated oils, and various emulsifying agents

Edwards[19] lists the following fats, oils, fatty acids and waxes which are official with the *United States Pharmacopoeia* and the *National Formulary*

Oleum Amygdalae Expressum U S P (expressed oil of almond), Oleum Chaulmoograe U S P (chaulmoogra oil), Oleum Gossypii Seminis U S P (oil of cottonseed), Oleum Lini U S P (linseed oil), Oleum Maydis U S P (corn oil), Oleum Morrhuae U S P (cod liver oil), Oleum Olivae U S P (olive oil), Oleum Ricini U S P (castor oil), Oleum Sesami N F (sesame oil),

[18] For information on candle manufacture see E Schlenker in Hefter Schonfeld, *Chemie und Technologie der Fette und Fettprodukte*, Vol II, Springer, Vienna, 1937, and also L W Geller, *Oil & Soap*, **12**, 262 265 (1935)

[19] L D Edwards, *Oil & Soap*, **17**, 82 84 (1940)

Oleum Tiglii N F (croton oil), Acidum Oleicum U S P (oleic acid), Acidum Stearicum U S P (stearic acid) Adeps (lard), Adeps Benzoinatus (benzoinated lard), Adeps Lanae (wool fat), Adeps Lanae Hydrosus (hydrous wool fat or lanolin), Oleum Theobromatis (cocoa butter), Sevum Preparatum (prepared suet), Cera Alba (white wax), Cera Flava (yellow wax) and Cetaceum (spermaceti) are all U S P materials

In pharmaceutical preparations, oils and fats are used as emollients and as carriers for medicinal substances to be applied to the skin Castor oil and croton oil are used as cathartics, and chaulmoogra oil is used in the treatment of leprosy The use of cod liver oil and other fish liver oils as sources of vitamins A and D is of course well known Oils such as corn oil, sesame oil, and cottonseed oil are employed as carriers for vitamin concentrates and other fat soluble substances

Cocoa butter has the property of remaining firm at ordinary temperatures, but melting at the temperature of the body, hence is a standard base for suppositories

5 Polishes

Polishes for furniture, floors, automobiles, leather, metal, etc usually have a wax base, although fatty materials are common minor ingredients in formulas for these products [20] The fats and fatty acids most used are commercial stearic and oleic acids, linseed oil, and castor oil

6. *Insecticides*

Fatty oils are used in insecticide sprays in the form of soaps or other surface active materials, as wetting and spreading agents Oils as such are used to promote adhesion of the spray in the "inverted spray" method of Marshall[21] for the control of the codling moth The oils employed are exclusively fish oils, principally because of the low cost of these

In some cases fats or fatty derivatives may in themselves be toxic agents for insects Soaps have been found to be effective against some insects,[22] although in practice they are used only as adjuncts to other and more potent insecticides Ralston, Barrett, and Hopkins[23] have found certain fatty amines to be effective against houseflies, and have suggested dioctyl amine as a substitute for pyrethrum in household insect sprays Sesame oil is used as an addition agent to some insect sprays because of the synergistic action of its unsaponifiable materials with pyrethrum [24]

[20] See, for example, H Bennett, *Practical Emulsions* Chemical Pub Co New York, 1943

[21] J Marshall *Wash Agr Expt Sta Tech Bull No 350* 1-88 (1937)

[22] F Tattersfield and C T Gimingham *Ann Applied Biol*, 14, 217-239 (1927) W E Fleming and F E Baker, *J Agr Research* 49, 29-38 (1934)

[23] A W Ralston, J P Barrett and E W Hopkins, *Oil & Soap* 18, 11-13 (1941)

[24] H L Haller, E R McGovran, L D Goodhue, and W N Sullivan, *J Org Chem*, 7, 183-184 (1942)

Fatty oils, and particularly fish oil, are used in the preparation of sticky, weatherproof tree banding compounds, used to prevent infestation of trees by larvae from the ground

7. Tinning Oils

Normally, from 20 to 40 million pounds of palm oil are used annually in the United States in the manufacture of tin plate and cold reduced sheet steel

In tin plating, a thick layer of the oil is placed over the molten tin in the exit section of the plating bath to protect the tin from oxidation The oil also absorbs metallic oxides and flux residues, and serves to maintain the tin coating in a molten condition as the metal sheets emerge from the metal bath, it thus assists in producing upon the sheets a uniform coating In terne plating, from a tin-lead bath, a coating of oil serves a similar purpose, although some terne plating is carried out in a single bath with only a flux covering the molten metal

In the cold reduction process, the oil serves simply as a lubricant

Crude palm oil is used to the practical exclusion of other oils in tinning because it is relatively cheap, and has a composition near the optimum for the purpose The oil used must not be very unsaturated, else it will polymerize too rapidly at the high temperature (460–550°F) of the bath On the other hand, a certain degree of heat degradation in the oil is desirable, since it produces compounds which assist in dissolving metallic oxides, and promote uniform wetting of the metal by the oil

Bauer and Markley,[25] as a result of laboratory tests on different oils, have recommended hydrogenated cotton seed oil with an iodine value of about 50 as a substitute for palm oil in tinning, suggesting that the longer useful life of this oil would compensate for its higher cost, as compared with palm oil

8. Hydraulic Oils

Castor oil is extensively used as a base for fluids for hydraulic systems, and particularly those exposed to low temperatures, as for example automobile brake systems and those used for various purposes on airplanes Castor oil has certain advantages over mineral oils and other fatty oils, it has a relatively low cold test, is compatible with polar liquids of low viscosity, and has little effect on rubber gaskets

The compounding of castor oil base hydraulic fluids is discussed by Shough,[26] who recommends higher aliphatic alcohols as the other principal ingredient, and the use of bodied, rather than raw, castor oil, to obtain a mixture of reasonably high viscosity, but low cold test

[25] S T Bauer and K S Markley, *Oil & Soap*, 20, 1–11 (1943)
[26] A H Shough, *Ind Eng Chem*, 34, 628–632 (1942)

9. Commercial Fatty Acids

Although the characteristics and uses of the commercially available fatty acids are mentioned in various other places in this book, it appears desirable to make a recapitulation here of the data pertaining to this important class of fatty materials

The products commonly known as oleic and stearic acids have for many years been made by fractionally crystallizing and pressing the mixed fatty acids from inedible tallow This operation merely produces a reasonably close separation of the saturated and unsaturated acids in the mixture, hence these acids are by no means pure or even fairly pure compounds Actually, commercial stearic acid contains slightly more palmitic acid than stearic, the ratio of the two acids being about 55 to 45 In addition to these two saturated acids, it also contains from 2% to 8% unsaturated acids, consisting principally of oleic, with a trace of linoleic acid Commercial oleic acid usually contains not more than about 70% actual oleic acid, the impurities consisting of the above mentioned saturated acids and linoleic acid, in approximately equal proportions

Stearic and oleic acids are made in so called saponified and distilled grades, according to whether the fatty acid stock is taken directly from the splitting equipment, or distilled before pressing Considerable purification of the acids is obtained by distilling, on the other hand saponified acids are usually made from higher grade materials than distilled acids, and are not necessarily inferior in quality

In 1929 the United States Bureau of the Census reported the manufacture of 42,902,304 pounds of oleic acid, and 33,195,528 pounds of stearic acid

Stearic acid is single , double , or triple pressed, according to the hardness and degree of unsaturation desired Average melting points of single , double , and triple-pressed stearic acids are respectively about 125–126°, 128–129, and 130–131°F Iodine values of the three grades average about 15, 8, and 3, respectively, whereas average titers are approximately 53 2°, 54 2°, and 55 2°C Good stearic acid is white or only slightly yellowish in color, has a characteristic tallowy, but not strong odor, and is pulverulent and only slightly waxy in consistency It shrinks markedly upon solidification

Oleic acid, otherwise known as red oil, is always colored to some degree, the depth of color in good samples varying from light straw to a deep red or reddish brown Acid which has become slightly contaminated with iron may be nearly black The iodine value of commercial oleic acid is usually between about 85 and 95, and very often is quite close to 90, which is the iodine value of the pure acid However, this is only due to the saturated and linoleic acid impurities being present in approximately equal proportions The titer of commercial oleic acid is ordinarily a little below that of pure oleic acid, being usually not greater than about 10°C

So called "vegetable oleic acid" consists simply of the mixed fatty acids of a vegetable oil, with the higher melting portions removed This product, which is usually made from vegetable oil foots, contains much more lineoleic acid than ordinary commercial oleic acid

By completely hydrogenating a vegetable oil and then splitting it, a product can be obtained which consists predominantly of stearic acid, with a small amount of palmitic acid, and negligible amounts of unsaturated acids The percentage of stearic acid in such a product may be as high as about 90%, if the starting material is soybean oil, corn oil, or sunflowerseed oil, and the titer may be as high as about 65°C However, this type of stearic acid is made in much smaller quantities than that from tallow

Stearic acid of high purity can also be made by fractional distillation of fatty acid mixtures A commercial product of this class contains 90% stearic acid, with about 6% palmitic and 4% oleic acids, and has an iodine value of 3 0, and a melting point of 67 0°C A mixture of 29% stearic acid, 67% palmitic acid, and 4% oleic acid is marketed as the true eutectic mixture of stearic and palmitic acids It has a titer of 54°C, and is claimed to be distinctively firm and waxy

For the production of reasonably pure saturated acids other than stearic, resort must also be made to fractional distillation The following specifications for commercially available distilled acids are taken from the literature of a prominent manufacturer [27] Palmitic acid iodine value, 3, mean molecular weight, 258, melting point 56°C , contains approximately 90% palmitic acid, 6% stearic acid, and 4% oleic acid Myristic acid iodine value, 2, mean molecular weight, 226, melting point 51°C , contains 90% myristic acid, 4% lauric acid, 4% palmitic acid, and 2% unsaturated acids Lauric acid iodine value, 1, mean molecular weight, 203, melting point, 37 8°C , contains 90% lauric acid, 9% myristic acid, a trace of capric acid, and 1% unsaturated acids Capric acid iodine value, 1, mean molecular weight, 173, melting point, 30°C , contains 90% capric acid, 7% lauric acid, 3% caprylic acid, and a trace of unsaturated acids Caprylic acid iodine value, 1, mean molecular weight, 146, melting point, 13 0°C , contains 90% caprylic acid, 3% caproic acid, 7% capric acid, and a trace of unsaturated acids

Among the more important manufactured products in which fatty acids are used are soaps, lubricating greases, alkyd resins, miscellaneous surface-active materials, polishes and buffing compounds, candles cosmetics, and rubber tires In the latter product stearic acid acts as a plasticizer, and also in the form of zinc stearate, it performs a chemical function in controlling the vulcanization of the rubber

[27] *Neo Fat New Fatty Acids and Oils for Industrial Purposes* Armour and Co, 1943

9. Commercial I...

Although the characteristics and u... fatty acids are mentioned in various ... desirable to make a recapitulation here ... tant class of fatty materials.

The products commonly known as ... years been made by fractionally cryst... acids from inedible tallow. This op... close separation of the saturated a... hence these acids are by no means ... Actually, commercial stearic acid co... stearic, the ratio of the two acids ... these two saturated acids, it also ... acids, consisting principally of olei... mercial oleic acid usually contain... *acid, the impurities consisting of t*... linoleic acid, in approximately eq...

Stearic and oleic acids are m... grades, according to whether th... the splitting equipment, or distill... tion of the acids is obtained by d... are usually made from higher ... are not necessarily inferior in ...

In 1929 the United States ... facture of 42,902,304 pounds of ... acid.

Stearic acid is single-, double ... and degree of unsaturation ... double-, and triple-pressed st... 128–129, and 130–131°F. ... about 15, 8, and 3, respecti... 53.2°, 54.2°, and 55.2°C. Go... ish in color, has a character... verulent and only slightly ... upon solidification.

Oleic acid, otherwise kno... the depth of color in good ... or reddish brown. Acid ... iron may be nearly blac... usually between about 85 ... is the iodine value of th... saturated and linoleic ac... proportions. The titer ... that of pure oleic acid, ...

... hydrocarbons is said to ... 1939, and has undoubtedly

... the properties of these ... Vitka,[23] from whom the

... water gas by the Fischer- ... The crude paraffins, ... varying molecular weights, ... *paraffins of about 19* ... treatment. It is necessary to ... *approximately twice the length*

... an oxidizing pre-treatment ... potassium permanganate or ... 150°C. for a brief period,

... Acids

...	26.2°C.
	Practically none
...	244.2
...	247.2
...	229.8
...	4.9
...	3.7
...	0.0
...	0.29

... The pre-tre... to ... must be ...

... with air in

material remaining after saponification The crude fatty acids obtained by splitting the resulting soaps with mineral acid are purified by extraction with various solvents and fractional distillation The latter operation also serves to select the fatty acids of medium molecular weight which are desired in the finished material The analysis in Table 133 is quoted for a typical product The product consists practically entirely of straight chain saturated acids, the production of branched chain acids is said to be negligible The following typical composition (in per cent) is listed C_8, 0 4, C_9, 2 1, C_{10}, 5 0, C_{11}, 7 3, C_{12}, 13 9, C_{13}, 16 3, C_{14}, 15 2, C_{15}, 12 4, C_{16}, 8 1, C_{17}, 7 3, C_{18}, 3 5, C_{19-21}, 7 3, and C_{22}, 1 2

The synthetic fatty acids have presumably been used so far only for soapmaking and similar purposes However, after esterification with glycerol they are said to be biologically and nutritionally equivalent to natural fats of equivalent molecular weight

10 Synthetic Fatty Acids and Fats

The production of synthetic fatty acids from hydrocarbons is said to have amounted to 40,000 tons in Germany in 1939,[28] and has undoubtedly increased greatly since

The manufacture of synthetic fatty acids and the properties of these materials have been discussed in some detail by Wittka,[28] from whom the following is taken

Synthetically prepared paraffins prepared from water gas by the Fischer-Tropsch process are employed as the raw materials The crude paraffins, consisting of a mixture of members of widely varying molecular weights, are fractionally distilled and the portion comprising paraffins of about 19 to 28 carbon atoms is reserved for further treatment It is necessary to employ paraffins with hydrocarbon chains approximately twice the length of the fatty acids desired

The selected paraffin stock is subjected to an oxidizing pre treatment involving mixing with about 0 1% powdered potassium permanganate or other chemical oxidizing agent, heating to about 150°C for a brief period,

TABLE 133
ANALYSIS OF SYNTHETIC FATTY ACIDS

Solidification point	26 2°C
Odor	Practically none
Acid value	244 2
Saponification value	247 2
Average molecular weight	229 8
Iodine value	4 9
Hydroxyl value	3 7
Naphtha insoluble, %	0 0
Unsaponifiable matter, %	0 29

and then blowing with air at about 100°C The pre-treatment serves to initiate the formation of peroxides, which must be present for the subsequent stage of oxidation to proceed rapidly

After pretreatment, the stock is blown with air in towers of special design, until 30% to 50% of the paraffins have been oxidized to form acids A catalyst consisting of manganese soaps amounting to 0 5% to 1 0% of the weight of the stock is employed The operation is carried out at a temperature of about 100°C, and requires in the neighborhood of 24 hours In the course of oxidation, rupture occurs more or less at random along the hydrocarbon chains, hence a mixture of fatty acids of different chain lengths is formed, in addition to a great variety of other decomposition products

The fatty acids and other acidic substances formed in the oxidized stock are separated from a high proportion of unsaponifiable material by saponifying the mass with sodium carbonate, and discarding the water insoluble

[28] F Wittka, *Soap Sanit Chemicals*, **16**, No 8, 28 32, 73 (1940)

material remaining after saponification The crude fatty acids obt by splitting the resulting soaps with mineral acid are purified by extra with various solvents and fractional distillation The latter operatio serves to select the fatty acids of medium molecular weight whic desired in the finished material The analysis in Table 133 is quot a typical product The product consists practically entirely of st chain saturated acids, the production of branched chain acids is said negligible The following typical composition (in per cent) is l C_8, 0 4, C_9, 2 1, C_{10}, 5 0, C_{11}, 7 3, C_{12}, 13 9, C_{13}, 16 3, C_{14}, 15 2, C_{15}, C_{16}, 8 1, C_{17}, 7 3, C_{18}, 3 5, C_{19-21}, 7 3, and C_{22}, 1 2

The synthetic fatty acids have presumably been used so far on soapmaking and similar purposes However, after esterification glycerol they are said to be biologically and nutritionally equivale natural fats of equivalent molecular weight

D. UNIT PROCESSES IN OIL AND FAT TECHNOLOGY

CHAPTER XV

EXTRACTION OF FATS AND OILS

1. Introduction

The separation of oils and fats[1] from oil bearing animal and vegetable materials constitutes a distinct and specialized branch of fat technology The widely differing characteristics of different fatty materials have given rise to such diverse extraction processes as rendering, pressing, and solvent extraction However, all extraction processes have certain objects in common These are, first, to obtain the oil uninjured and as free as possible from undesirable impurities, second, to obtain the oil in as high a yield as is consistent with the economy of the process, and third, to produce an oil cake or residue of the greatest possible value

Fatty animal tissues consist largely of fat and water, which may be separated from the solid portions of the tissue and from each other with relative ease, by one of the rendering processes The extraction of vegetable oils is a more difficult matter Vegetable materials, and in particular some of the oil seeds, contain a large proportion of solid material associated with the oil Careful reduction of the material, followed by heat treatment and the application of heavy pressure, is required to obtain an efficient separation of the oil from the solids

Even after the most efficient pressing, an oil cake will retain an appreciable amount of absorbed oil, the latter will usually amount to 4–7% of the weight of the cake In the case of seed or other materials initially high in oil and low in solids content, the unextracted residue will be but a small fraction of the total oil However, in seeds of low oil content, as, for example, soybeans, it may constitute as much as 20–25% of the oil For the processing of low oil seeds, solvent extraction is particularly valuable, since it will reduce residual oil in the extracted seeds to less than 1% The chief disadvantages of solvent extraction are the high initial cost of the

[1] GENERAL REFERENCES H N Brocklesby, *The Chemistry and Technology of Marine Animal Oils*, Fisheries Res Board of Canada, Ottawa, 1941 R Heublyum and H Japhe, *Allgem Oel u Fett Ztg* 32, 401–405, 447–452, 497–502 (1935), 33, 13–17, 49–55, 96–103, 141–149 199–203, 254–261 (1936) K S Markley and W H Goss *Soybean Chemistry and Technology*, Chemical Pub Co, New York, 1944 G Hefter and H Schönfeld, *Chemie und Technologie der Fette und Fettprodukte*, Vol I, *Chemie und Gewinnung der Fette*, Springer, Vienna, 1936 M K Thornton, Jr, *Cottonseed Products* Oil Mill Gazetteer, Wharton, Texas, 1932 W R Woolrich and E L Carpenter, *Mechanical Processing of Cottonseed*, Engineering Expt Sta, Univ of Tennessee, Knoxville, 1935

equipment, and the circumstance that some oil seeds are inclined to disintegrate under the influence of the solvent, and consequently are difficult to handle

There are a number of more or less critical operations in oil milling which are auxiliary to the actual expression or extraction Wherever possible it is desirable to decorticate oil seed before the oil is removed in order both to increase the capacity of the extraction equipment and to avoid loss of oil through absorption by the hulls The seeds must then be ground, or otherwise reduced to fine particles After they are reduced, they must be given heat treatment, to make the walls of the oil cells permeable to the oil and to render the oil free flowing In addition, oil milling or extraction presents problems in the handling and storage of the oil bearing materials, since these are prone to deteriorate, through oxidation, or bacterial or enzyme action

2 Storage and Handling of Oil-Bearing Materials

Animal fats are almost invariably rendered within a few hours after the animals are killed The only animal fats not so rendered are salt lard and other lards derived from cured pork cuts, and certain inedible tallows and greases, all of which are low grade products Even where there is no question of bacterial spoilage of the fatty stock, there will inevitably be enzyme action, almost from the moment of the death of the animal Edible animal fats, such as lard and oleo oil, are not usually refined for reduction of their free fatty acid content, consequently it is particularly important for rendering to be conducted promptly, before the free acids have become excessively high Since the enzymes responsible for fat splitting are quickly inactivated by moderately elevated temperatures, it is good practice to charge the fatty stock to the rendering apparatus as quickly as it is available The application of heat will arrest hydrolysis, even though the actual rendering operation may be somewhat delayed It is possible to produce animals fats with a free fatty acid content of 0 15% or less from very fresh stock However, oleo oil and lard usually contain 0 2% to 0 5% of free acid Edible tallow often contains 0 5% to 1 5% of free acids, and inedible tallows and greases may run as high as 40% or 50% in free fatty acids

Marine oils are also usually rendered from fairly fresh stock It is particularly injurious to the quality of the oil to allow fish to deteriorate before they are processed, because of the powerful proteolytic enzymes present in this class of material Fish oil in contact with decomposing proteins absorbs appreciable quantities of nitrogenous compounds which appear to enter actually into chemical combination with the oil [2] Combined nitrogen in the oil contributes greatly to undesirable color, flavor, and odor

[2] W L Davies, and E Gill, *J Soc Chem Ind*, 55, 141–146T (1936)

The high moisture content of palm fruits and olives, like that of animal tissues, is favorable to enzyme action, hence these materials must be processed promptly if they are to yield oil of low free fatty acid content. Palm fruits are particularly susceptible to deterioration. Their lipolytic enzymes are so active that even under the most favorable conditions palm oil is seldom produced with a free fatty acid content of less than 2% or 3%, and under crude conditions of processing the free acid content of this oil may be as high as 20%, 40%, or even 60% or more. According to Barnes,[3] the lipolytic enzyme of palm fruit is destroyed by a temperature of 55°C. Enzyme action is slow in freshly cut, undamaged bunches of fruit, but becomes extremely rapid if the fruits are bruised. It is virtually impossible to harvest the fruit bunches without some slight damage. According to the best practice,[4] all fruit bunches are "sterilized" by exposure to open steam as soon as possible after harvesting. The sterilization treatment serves the dual purpose of inactivating the enzymes and loosening the fruits to permit threshing from the stalks. Olives are less liable to lipolytic action. They are more or less bruised in harvesting and are often stored for days before they are processed, but such treatment is detrimental to the quality of the oil, which seldom contains less than 1% free fatty acids, and often runs as high as 5% or more.

Oil seeds are much less subject to deterioration than the materials of high moisture content mentioned above, and under suitable conditions may be stored for long periods before they are processed. However, there is a somewhat critical moisture level above which oil seeds do not keep well. The moisture content of seeds as they are received for storage may exceed this level, consequently the better equipped mills are generally provided with dryers to reduce the moisture in wet seeds before they are put into storage. The dryers are usually of continuous design, consisting of oil-, gas-, or coal-fired furnaces coordinated with a blower system to force hot air or flue gases and then cooling air through an incoming stream of the material to be dried. Complete drying of the seeds is not required; it is only necessary to reduce the moisture below the level mentioned above. Often this will not involve removal of more than a minor fraction of the total moisture.

The development of free fatty acids in the oil contained in wet seeds is paralleled by respiratory processes which evolve heat. In large masses of seed this heat is not readily dissipated, so that the temperature of deteriorating seed is inclined to rise. The rise in temperature may in extreme cases be sufficient to initiate thermal decomposition of the seed. In less severe cases it greatly accelerates the deteriorative processes,

[3] A. C. Barnes, "Chemical Investigations into the Products of the Oil Palm," Nigeria Dept. Agr. *Special Bull.* (1924).

[4] B. Bunting, C. D. V. Georgi, and J. N. Milsum, *The Oil Palm in Malaya*, Dept. Agr., Straits Settlements and Federated Malay States, Kuala Lumpur, 1934.

which in turn generate additional heat, so that the process, once started, is inclined to be self catalytic Cottonseed are particularly liable to heating These seed are invariably stored in the undelinted condition Their covering of fibers readily absorbs and retains moisture, and in addition acts as an efficient heat insulator Cottonseed storage houses are preferably provided with means for measuring the temperature of the seed mass in all parts, as well as blowers and ducts for the forced circulation of air through the seed, so that seed which show a tendency to heat can be quickly cooled

The relationship between moisture content and rate of free fatty acid increase in cottonseed has often been pointed out Of the observations made on seeds stored under commercial conditions, those of Robertson and Campbell[5] are typical They indicate that cottonseed with a moisture content of less than about 11% will not increase unduly in free fatty acids during prolonged storage Stored seed containing more than 14% moisture will invariably develop free acids very rapidly Between 11% and 14% moisture, the deterioration of the seed is variable

Karon and Altschul[6] have investigated the kinetics of free fatty acid development in cottonseed stored in the laboratory under controlled conditions Their results show the reaction to have the appearance of being autocatalytic, since its rate can be represented by the equation

$$dF/dt = kF(100 - F)$$

where t represents storage time, and F is the per cent free fatty acids in the oil The value of k, the rate constant, was determined on the same sample of seed at different moisture levels within the range of 7 5% to 20%. At moisture levels up to about 15% on the basis of the dry seed, or 13% on the basis of the moist seed, it increased but slightly with increasing *moisture content, but beyond this point it rose very sharply* The evidence presented by these authors points very definitely toward a lipolytic enzyme system as the cause of free fatty acid increase, even though Olcott and Fontaine[7] were unable to find a lipase in cottonseed by application of the usual methods of detection

Other seeds have been less carefully investigated but from such evidence as is available it appears that the behaviour of oil seeds in general must be quite similar to that of cottonseed The critical moisture content for rapid deterioration is somewhat different for different oil seeds, if expressed upon the basis of the whole seeds, but if it is calculated upon the more rational basis of the hygroscopic or nonoil portion of the seed kernel, within which an enzyme system must necessarily be operative, it tends to approach

[5] F R Robertson and J G Campbell, *Oil & Soap*, 10, 146–147 (1933)
[6] M L Karon and A M Altschul, *Plant Physiol*, 19, 310–325 (1944)
[7] H S Olcott and T D Fontaine, *Oil & Soap*, 18, 123–124 (1941)

a common value for all seeds The critical moisture content of 13% for whole cottonseed, which was mentioned above, corresponds to about 10 5% moisture in the seed kernel, due to the fact that the lint and hull retain water more readily than the kernel Since the kernels consist of about 30% oil and 70% nonoil substances, the critical 10 5% of the whole seed becomes 15% on the basis of the hygroscopic or nonoil portion of the seed Ramstad and Geddes[8] concluded from a series of adiabatic respiration studies that soybeans are not liable to heat badly in storage unless their moisture content exceeds 15%, although mill operators generally prefer not to store beans containing more than 13% moisture Moisture contents of 13% and 15% on the whole seed correspond to about 16% and 18%, respectively, on the basis of the nonoil portion of the seed It is stated[4] that palm kernels must be dried to a moisture content of 8% before they are bagged and shipped, in order to avoid deterioration This content of moisture amounts to about 15 5% of the nonoil portion of the kernel

Seeds whose cell structure has been damaged develop free fatty acids very rapidly Thus, for example, rolled cottonseed meats deteriorate markedly within a few days or even hours For this reason undecorticated seeds have much better storage properties than decorticated seeds It is observed that an oilseed which has been cut or fractured cleanly is much less inclined to develop free acids than seed which have been bruised or crushed This is particularly noticeable in the case of palm kernels, babassu kernels, or other large oil seeds

Much damage to oil seeds occurs in the field, over this phase of deterioration the oilseed processor of course has no control Field damage is usually the result of a delay in harvesting, during which the matured seeds are exposed to dampness However, field damage can also occur through interruptions in the normal development of the seeds prior to harvesting, such as may be caused by weather abnormalities The relation between weather conditions during the latter stages of cottonseed development and the quality of the oil in the seed has been discussed by Meloy [9]

Deterioration in oil seeds is manifested in other respects than partial hydrolysis of the oil There are associated changes in nonoil constituents of the oil which may greatly affect the quality of the oil In both cottonseed and soybeans there is an increase in the content of oil-soluble pigments, which causes the oil to be difficult to refine and bleach to a usable color There are obscure changes involving the solubilization of phosphatides or other surface active substances in the oil, possibly from the splitting of protein–phosphatide complexes, which may increase the refining loss out of proportion to the increase in free fatty acids However, not all changes occurring in stored oil seeds are undesirable The yield of oil from newly

[8] P E Ramstad and W F Geddes, Minn Agr Expt Sta *Tech Bull* 156 (1942)
[9] G S Meloy, *Oil & Soap*, 16, 172–178 (1939)

harvested soybeans is less than from the same beans after a period of storage[10] The storage of soybeans also results in a diminution in the chlorophyll content of "green beans" Chlorophyll in the oil is undesirable because of the difficulty of removing green color in subsequent processing, and because of the tendency of the color to become intensified by hydrogenation

Recently Altschul and co workers[6,11] have described a simple means of arresting free acid development in cottonseed, which possibly may serve as an alternative to drying as a means of conditioning high moisture seed for storage Their method comprises treating the seed with ammonia gas in sufficient amount to raise the pH of the seed from a normal value of about 6 0–7 0 to over 8 0 Treatment with hydrogen chloride gas, to decrease the *p*H to 5 0 or lower, is also effective but is less practicable The mechanism through which the ammonia or acid treatment operates has not been explained, but it presumably involves the inactivation or paralysis of an enzyme system

3 Grading of Oil Seeds and Calculation of Oil Yields

More or less elaborate grading systems have been developed in the United States for determining the value of the major oilseeds These systems may be divided into two categories (*a*) those which aim at establishing the general quality of the seeds, upon the basis of their soundness, their moisture content, and their freedom from foreign matter, and (*b*) those which are intended to evaluate the oil seeds more exactly, on the basis of the yield and quality of the oil obtainable from them Obviously the latter method of grading and valuation is the more rational, but it requires a chemical analysis of all seed samples and hence is not practicable in all cases

Under the provisions of the United States Grain Standards Act, all soybeans and flaxseed sold by grade in interstate or foreign commerce must be graded by licensed inspectors in conformity with established standards The present standards[12] applicable to these two seeds are listed in Tables 134 and 135

The trading rules of the National Cottonseed Products Association[13] provide a complete system for grading cottonseed upon the basis of their composition, and also specify methods of analysis for cottonseed, peanuts,

[10] K S Markley and W H Goss, *Soybean Chemistry and Technology* Chemical Pub Co, New York, 1944

[11] A M Altschul M L Karon, L Kyame, and M Caravella, *Oil & Soap* 20, 258–262 (1943)

[12] U S Agricultural Marketing Service, *Handbook of Official Grain Standards of the United States* Washington, D C, 1941

[13] National Cottonseed Products Association, *Rules Governing Transactions between Members* (1944–1945)

and soybeans, and standard formulas for the calculation of oil and of oil-cake yields.

TABLE 134

GRADE REQUIREMENTS FOR YELLOW SOYBEANS, GREEN SOYBEANS, BROWN SOYBEANS, BLACK SOYBEANS, AND MIXED SOYBEANS

Grade No	Minimum test weight per bushel lbs	Maximum limits of			
		Moisture, %	Splits, %	Damaged kernels (soybeans and other grains), %	Foreign material other than dockage, %
1[a]	56	13	10	2	1
2[a]	54	14	15	3	2
3	52	16	20	5	3
4[b]	49	18	30	8	5
Sample grade	Shall include soybeans of any of the classes Yellow Soybeans, Green Soybeans, Brown Soybeans, Black Soybeans, or Mixed Soybeans, which do not come within				

[a] The soybeans in Grade No 1 of each of the classes Yellow Soybeans and Green Soybeans may contain not more than 2%, and the soybeans in Grade No 2 of each of these classes may contain not more than 3% of Black, Brown, or bicolored soybeans, singly or combined

[b] Soybeans that are badly weathered or badly stained shall not be graded higher than No 4

TABLE 135

GRADE REQUIREMENTS FOR FLAXSEED

Grade No	Minimum test weight per bushel, lbs	Maximum limits of damaged flaxseed, %
1	49	20
2	47	30
Sample grade	Shall include flaxseed which does not come within the requirements of either of Grades No 1 or No 2; or which contains fire-damaged flaxseed, or which contains more than 11% of moisture, or which is musty, or sour, or heating, or hot, or which has any commercially objectionable foreign odor, or which is otherwise of distinctly low quality.	

Under the N C P A. rules, a "Quantity Index" for cottonseed is established as follows:

(*a*) For cottonseed that by analysis contain 17% or more of oil, the Quantity Index shall equal 4 times the percentage of oil, plus 6 times the percentage of ammonia, plus 5

(*b*) For cottonseed that by analysis contain less than 17% of oil, the Quantity Index shall equal 5 times the percentage of oil, plus 6 times the percentage of ammonia, minus 12

A "Quality Index" is also established For cottonseed which have a Quantity Index of not less than 103, and which contain not more than 0 5% foreign matter, not more than 0 5% free fatty acids in the oil, and between 9% and 10% moisture, the Quality Index is 102 Seed which contain not more than 3% foreign matter, not more than 12% moisture, and not more than 1 8% free acids in the oil have a Quality Index of 100 In the case of cottonseed which fail to meet the requirements for a Quality Index of 100, the Quality Index is reduced below 100 according to the following scheme (*a*) 0 5 unit is deducted for each 0 1% free fatty acid in excess of 1 8%, (*b*) 1 0 unit is deducted for each 1 0% of foreign matter in excess of 3%, and (*c*) 1 0 unit is deducted for each 1 0% of moisture in excess of 12% A numerical grade (to the nearest 0 5 unit) is then assigned to the cottonseed according to the following equation

$$\text{Grade} = \frac{(\text{Quality Index})(\text{Quantity Index})}{100}$$

The calculation of grade may be illustrated as follows [13]

Analysis of the seed

Oil	19 0%
Ammonia	3 84%
Moisture	13 5%
Free acids	2 4%
Foreign matter	3 0%

Calculation of the Quantity Index

(4) (19 0) = 76 00
(6) (3 84) = 23 04
Plus 5 00
QUANTITY INDEX = 104 04

Calculation of the Quality Index

Reduction for free fatty acids in excess of 1 8%,
(6) (0 5) = 3 0 units

Reduction for moisture in excess of 12 0%,
(1) (1 5) = 1 5 units

Total reduction = 4 5 units
QUALITY INDEX = 100 minus 4 5 = 95 5

Calculation of the grade

$$\frac{(104\ 04)\ (95\ 5)}{100} = 99\ 36 \text{ or } 99\ 5$$

Cottonseed is quoted and sold on the basis grade of 100, with premiums or penalties being assessed for deviations above or below this grade In

TABLE 136[a]

The table shows the press room standards (per cent oil divided by per cent ammonia in cake) for varying ammonia percentages in seed It also shows the pounds of oil left in cake plus a constant of 4 pounds of oil left in hulls This weight of oil in cake for any given per cent ammonia in seed is a constant for cake of any ammonia content

Total ammonia	Available ammonia 94% of total	Press room standard	Pounds oil in 8% cake and hulls
2 80%	2 63%	87	50
2 85%	2 68%	87	50
2 90%	2 73%	86	51
2 95%	2 77%	86	51
3 00%	2 82%	85	52
3 05%	2 87%	85	53
3 10%	2 91%	84	53
3 15%	2 96%	84	54
3 20%	3 01%	83	54
3 25%	3 06%	83	55
3 30%	3 10%	82	55
3 35%	3 15%	82	56
3 40%	3 20%	81	56
3 45%	3 24%	81	56
3 50%	3 29%	80	57
3 55%	3 34%	80	57
3 60%	3 38%	79	57
3 65%	3 43%	79	58
3 70%	3 48%	78	58
3 75%	3 52%	78	59
3 80%	3 57%	77	59
3 85%	3 62%	77	60
3 90%	3 67%	76	60
3 95%	3 71%	76	60
4 00%	3 76%	75	60
4 05%	3 81%	75	61
4 10%	3 85%	74	61
4 15%	3 90%	74	62
4 20%	3 95%	73	62
4 25%	3 99%	73	62
4 30%	4 04%	72	62
4 35%	4 09%	72	63
4 40%	4 13%	71	63
4 45%	4 18%	71	63
4 50%	4 23%	70	63
4 55%	4 28%	70	64
4 60%	4 32%	69	64
4 65%	4 37%	69	64
4 70%	4 42%	68	64
4 75%	4 47%	68	65
4 80%	4 51%	67	65

[a] National Cottonseed Products Assoc *Rules Governing Transactions between Members* (1944–1945)

calculating the settlement price of the seed, the weight of the shipment is also determined on the basis of the analysis, being adjusted downward in proportion to the foreign matter in the seed, where the content of foreign

matter exceeds 1% Grade premiums or penalties are calculated on the basis of the weight so adjusted

The value of oilcake is dependent upon its protein content, which is customarily reported in terms of ammonia (NH_3), and calculated to protein, using the factor 6 25 in converting from nitrogen to protein Cottonseed or peanut cake or meal is commonly adjusted to a definite protein content at the mill by varying the completeness with which the hulls are separated from the meats or by adding ground hulls to the meal Cottonseed cake most commonly has a protein content of 41%, or an ammonia content of 8%, whereas peanut meal usually is sold as containing 45% protein or 8 76% ammonia The protein content of soybean meal is variable, since the beans are not decorticated in processing and no hulls are available for adjustment of the protein content Mechanically expressed soybean meal usually contains in the neighborhood of 43% protein, although solvent extracted meal may contain 50% or more

According to the N C P A formula[13] for the calculation of yields the ammonia available in cottonseed for the production of oilcake is considered to be 94% of the ammonia present in the whole seed The remaining 6% is lost in the hulls and in the dust, etc , incidental to milling operations The possible yield of oilcake of a definite ammonia content, from a ton of cottonseed is calculated from the ammonia content of the seed and the availability factor of 0 94 referred to above In the calculation of oil yields from cottonseed it is necessary to assume an arbitrary loss of oil in the oilcake It is customary to express the efficiency of oil extraction in terms of "press room standards" (per cent oil divided by per cent ammonia content of the seed) as indicated in Table 136 The available oil per ton of cottonseed is found by subtracting from the total oil in the seed the pounds of oil in the cake and hulls corresponding to the ammonia content of the seed, as shown in Table 136 As an example

Analysis of the seed

Ammonia	3 50%
Oil	18 6%

Calculation of cake yield

Available ammonia = (3 50%) (0 94) = 3 29%
Yield of ammonia per ton of seed = (0 0329) (2000) = 65 8 lbs
Yield of 8% ammonia cake per ton of seed = 65 8/0 08 = 822 lbs

Calculation of oil yield

Total oil per ton of seed = 372 lbs
Oil lost in cake and hulls (from Table 136) = 57 lbs
Available oil = 372 minus 57 = 315 lbs

In the case of peanuts, the first assumption is that there will be a loss of 5% of the original nuts in the milling operation The available ammonia

is assumed to be 92% of the ammonia in the whole nuts The yield of available ammonia is thus 0 95 times 92% of the total ammonia In the calculation of the oil yield, the amount of oil in the nuts is first discounted 5% as an allowance for the milling loss A press room standard of 0 80 is assumed, so that the oil lost in the cake is calculated as being equivalent to the yield of cake times the per cent ammonia in the cake, times 0 80, divided by 100 An additional 6 pounds of oil per ton of peanuts is considered to be lost in the hulls, and finally it is assumed that there is an "invisible loss" of 3% of the total oil in milling Thus the available oil per ton of peanuts is as follows

lbs available oil per ton of nuts =
[(lbs total oil) (0 95) − (lbs oil lost in cake) − 6] 0 97

In the calculation of oil and cake yields in soybean milling by the N C P A formula it is assumed that the cake will contain 7 5% moisture and 5 0% oil, and that the loss of material in milling will be negligible Such a calculation is of course not applicable to the solvent extraction of soybeans

In well operated cottonseed and peanut mills the yields calculated as above are commonly exceeded by a substantial margin, particularly in the milling of peanuts

4. Mechanical Pretreatment of Oil-Bearing Materials

(a) *Preparation of Animal Materials*

Fatty animal materials, as compared with oilseeds and other vegetable materials, require comparatively little preparation prior to the rendering operation Fatty stock destined for the production of neutral, low-temperature rendered fats, such as oleo stock or lard, is trimmed quite carefully, and washed before it is charged to the rendering units Ordinary stock, such as that used in making prime steam lard, is not always washed and is less carefully trimmed

In the larger establishments the stock to be rendered is sorted into different classes of material, partly in order to avoid mixing high quality materials with those of low quality, and partly because some stocks, such as those containing large bones, require more severe rendering treatment than others

Rotary hashers, similar in principle to ordinary household food choppers, are used for the reduction of stock which is free from bones The degree of reduction is much coarser than that employed in the processing of oil seeds, the dimensions of the hashed pieces may be measured in large fractions of inches or even in inches Most animal materials disintegrate quite readily Whale blubber is particularly tough and requires more drastic treatment Blubber presses, consisting of heavy corrugated rolls,

are said to be now in use[14] Passage of large chunks of blubber through these rolls reduces them to semifluid condition, and decreases the rendering time

Stock which is to be dry rendered requires more thorough reduction than that which is to be rendered by a wet process Prolonged wet rendering under pressure will disintegrate even large bones or whole carcasses, so that the preparation of stock for this process is not extremely critical

(b) *Decortication of Oil Bearing Seeds*

Oil seeds are preferably decorticated before they are extracted, wherever this is practicable The hulls of oil bearing seeds are low in oil content, usually containing not more than about 1% oil An oil content of 22% has been reported[15] in the hull of the flaxseed However, this is not believed to represent a true value for the hull, it appears rather to be due to a part of the oily endosperm of the kernel remaining attached to the separated hull If the hulls are not removed from the seeds before the latter are extracted they merely reduce the total yield of oil by absorbing and retaining oil in the press cake, and in addition they reduce the capacity of the extraction equipment

The various palm kernels, such as oil palm or African palm kernels, babassu kernels cohune kernels, etc , constitute a particular class of oil seeds, since they are of relatively large size and are surrounded by a particularly hard, thick shell Due to the cheapness of labor in the producing regions, the large size of the nuts, and the refractory nature of the shells these nuts are often cracked and the kernels separated by hand Thus the entire production of Brazilian babassu kernels, amounting in some seasons to as much as 25,000 tons, has in the past been separated by hand

Nuts of the oil palm, which are less thick shelled than most of the American palm nuts, are apparently cracked to some extent by hand in Africa, but on the plantations of the East Indies and British Malaya they are usually cracked by machine In one type of machine the nuts are fed to the center of a rotor provided with curved baffles, along which the nuts are flung out against a heavy steel housing and broken by impact Another type of machine is simply a special type of hammer mill The rotor consists of a frame supporting four heavy steel paddles The nuts are dropped into the path of the paddles and cracked by impact After the nuts are cracked they are dropped to rotary screens, where some separation of kernels and shells is obtained A considerable proportion of shell fragments, however, cannot be separated by screening Owing to the high density of the shells, air separation, such as is used on cottonseed and

[14] H N Brocklesby, *The Chemistry and Technology of Marine Animal Oils* Fisheries Research Board of Canada Ottawa 1941

[15] G W Owen, *Oil & Soap*, **16**, 55-58 (1939)

peanuts, etc , is likewise ineffective in producing a further separation There are two methods in vogue for separating palm kernels from shell fragments of a size comparable to that of the kernels The dry method takes advantage of the fact that the kernels are rounded and inclined to roll easily, whereas the pieces of shell are flat and sharp edged, and hence do not as readily roll on an inclined surface Dry separators consist of inclined belts provided with sharp projections, which move continuously upward When a mixture of kernels and seeds is fed onto the surface of the belt, the kernels are inclined to roll down the belt, where they are collected at the lower end, whereas the fragments of shell are caught on the projections and carried over the top of the belt into a separate bin Means must be provided for recycling of material after both the cracking and separating operations, since neither cracking or separation is complete after one passage of the material through the machines

The alternative method of separation consists of floating the kernels from the more dense shells in brine solution The flotation method has the advantage of producing a clean separation of kernels and shells, but the kernels separated by this process must be dried before they can be stored or shipped

The American palm nuts of the *Attalea* family, including the babassu and cohune, are excessively thick shelled and most difficult to decorticate by machinery The babassu is particularly difficult because of the fact that it contains several kernels, each of which is enclosed in a separate cavity within the shell Whereas the splitting of an oil palm nut or most cohune nuts along a single plane of cleavage will usually free the kernel, the similar splitting of a babassu nut may not release a single one of its four to eight kernels Recently a number of different machines have been devised for cracking American palm nuts The machines designed for round nuts of the coyol type have either been of the centrifugal or hammer mill design, or have utilized the positive action of mechanically or hydraulically operated hammers striking against the nut as it is confined against a stationary anvil member Some of the machines designed for cohune or babassu nuts employ chisel like cutting edges to open the shell One type of babassu opening machine has opposed cutting edges which split the nut into a number of segments, like those of an orange Other machines for cohune and babassu nuts employ the hammer mill principal These machines break up the kernel rather badly, and thorough drying of the kernels is depended upon to inhibit excessive enzyme action in the broken kernels during shipment

In the case of any variety of palm nut, adequate drying of the nuts prior to cracking is highly essential to insure that the kernel will not adhere to the shell The kernels shrink considerably in drying and thus break away from the shell Green or undried kernels fill the shell cavity

tightly and adhere to the shell very strongly In Malaya the general custom is said to be to expose oil palm kernels to the air in layers 4 to 5 feet deep, in roofed sheds equipped with concrete floors[4] A month's drying under these conditions suffices for reasonably good cracking and separation, and six weeks' drying insures good separation Some factories use steam heated drying rooms, in which the nuts, contained on wire trays, are adequately dried in 3 days Another effective drying method is to treat the nuts with live steam in a revolving drum for 1 to 2 hours, after which they are air dried for a few hours Because of their thicker shells, American palm nuts such as the cohune and the babassu would be expected to dry more slowly Aside from the fact that it is necessary for efficient decortication, thorough drying of the nuts will of course minimize the danger of deterioration in the kernels from enzyme action

The hulling machines used for the decortication of medium size oil seeds with a flexible seed coat, such as cottonseed, peanuts and sunflower seed, are of two principal types bar hullers and disc hullers

The rotating member of a bar huller consists of a cylinder which is equipped on its outer surface with a number of slightly projecting, longitudinally placed, sharply ground, square edged knives or "bars" Opposed to the cylinder over an area corresponding to about one third of its surface is a concave member provided with similar projecting bars The seed are fed between the rotating cylinder and the concave member, and the hulls are split as the seed are caught between the opposed cutting edges The clearance between the cutting edges is of course variable for seeds of different size

The disc huller is more or less similar in principle to the bar huller, except that the cutting edges consist of grooves cut radially in the surfaces of two opposed and vertically mounted discs, one of which is stationary and the other rotating The seeds are fed to the center of the discs and are discharged at their periphery by centrifugal force With either type of huller the condition of the seed is somewhat critical Wet seed are difficult to split cleanly, and are inclined to clog the huller, particularly if it is of the disc type On the other hand, if the seed are very dry, the kernels are inclined to disintegrate to an excessive extent

Different seeds vary considerably in the readiness with which they fall out of the split hulls Peanuts, for example, are quite loose in the shell and separate readily Cottonseed kernels or "meats" are more adherent to the hull, consequently the hulls are customarily passed through a hull beater to detach small meat particles after the first separation of hulls and meats by screening The separation systems used for cottonseed, peanuts, etc, consist of various combinations of vibrating screens and pneumatic lifts It is necessary not only to separate the hulls from the meats, but also to separate and recycle a certain proportion of uncut seeds

which escape the action of the huller In the case of cottonseed the following separations are commonly carried out (*a*) separation of large meat particles from hulls and uncut seed by screening, (*b*) separation of hulls from uncut seed by an air lift, (*c*) separation of small meat particles from hulls by beating and screening, and (*d*) separation of hull particles from meats by air

In practical mill operation, the greatest yield of oil is obtained by nicely balancing the degree of separation attained If an attempt is made to separate hulls from the meats too cleanly, there will be a loss of oil due to meats being carried over into the hulls If an excessive proportion of hulls is left in the kernels there will likewise be an undue loss of oil from absorption by the hulls Under certain conditions, there may be an appreciable loss of oil due to absorption by the hulls as the latter come into contact with the oily meat particles during the separation operation It is generally advisable to effect the separation of kernels and hulls as quickly as possible after the seeds are hulled, in order to avoid excessive contact between hulls and kernels or kernel particles

There are a number of accessory operations in the decortication of small oilseeds The seed must be freed from dirt, sticks, leaves, and assorted trash before it is fed to the hullers Such cleaning is preferably carried out before the seed is placed in storage Cleaning equipment is quite variable in different mills and consists of various combinations of rotary screens, shaker screens, and pneumatic lifts Electromagnets should be placed somewhere in the line, before the hullers, to remove tramp iron For the cleaning of peanuts, special "stoners" must be provided for separation of the stones and mud balls commonly present in threshed nuts Stones cannot of course be removed completely by screening, but are easily separated from the seed by virtue of their much greater density

Cottonseed are invariably delivered to the mills from the gins without removal of their coating of short fibers or linters, and must be delinted before they are hulled Delintering machines (known as "linters") are similar in principle and appearance to cotton gins, consisting essentially of a revolving assembly of closely spaced circular saws which pick the lint from the seed A cylindrical brush revolving slightly faster than the saw assembly is provided to remove the lint from the saw teeth The lint is blown from the brush to the surface of a perforated "condenser" drum, and continuously removed from the surface of the drum in the form of a roll The lint is not ordinarily removed from the seed in a single operation, but is taken off in two or three cuts Each successive cut is of lower grade than the cut preceding it, since increasing quantities of hull material are removed by the saws as delinting proceeds

Soybeans are not decorticated before they are processed for oil, except in cases in which the meal is destined for human consumption, because the

hull constitutes but a small part of the seed and is relatively nonabsorbent. Small oil seeds, such as flaxseed, perilla seed, rapeseed, sesame seed, etc., are also processed without decortication. In some cases it would doubtless be desirable to hull the small seeds, if this could be done economically, but so far the process has been considered impracticable. Owen[15] has reported a series of experiments in the dry decortication of flaxseed and other small oilseeds, in an experimental machine of unspecified design. He concluded that hulling of linseed is impracticable because of the fact that a large

TABLE 137

APPROXIMATE PROPORTIONS OF HULL AND KERNELS IN DIFFERENT OIL SEEDS AND OIL CONTENTS OF THE WHOLE SEED, KERNELS, AND HULLS

Oil seeds	Per cent kernel	Per cent hull	Per cent oil in		
			Whole seed	*Kernel*	*Hull*
Usually decorticated					
Oil palm	25	75	—	48	—
Babassu	9	91	—	67	—
Cohune	10	90	—	67	—
Tucum	30	70	—	47	—
Murmuru	40	60	—	—	—
Tung	60	40	30	50	—
Oiticica	65	35	38	58	—
Cacao beans	88	12	50	—	—
Castor beans	70-80	20-30	40-50	—	—
Cottonseed (delinted)	62	38	19	30	1-2
Peanuts	75	25	38	50	0.5-1
Sunflowerseed	45-60	40-55	22-36	36-55	1.2
Kapok	60	40	20-25	40	—
Usually not decorticated					
Soybeans	93	7	18	—	0.6
Flaxseed	57	43	—	58	22
Perilla seed	68	32	34	—	—
Hemp seed	62	38	31	—	—
Rapeseed	82	18	42	—	—
Mustard seed	80	20	—	—	—

portion of the total oil is contained in the separated hull, but suggested that it might prove advantageous in the case of certain other small seeds, as for example, hempseed.

(c) *Reduction of Oil Seeds*

The extraction of oil from oil seeds, either by mechanical expression or by means of solvents, is facilitated by reduction of the seed to small particles.

Opinion appears to be more or less divided as to whether the grinding

or crushing of oil seed actually disrupts a large proportion of the oil bearing cells Woolrich and Carpenter[16] concluded from the microscopic examination of rolled cottonseed that there was little disruption of cells As an argument against extensive cell destruction they pointed out that the cells of cottonseed are but 0 001 to 0 0015 inch in diameter, whereas the thickness of rolled cottonseed particles is not less than 0 005 inch On the other hand, Goldovskii and Podol'skaia[17] and Shchepkina[18] have reported a destruction of cells in rolled oil seeds ranging from about 50% to as high as 83% The former workers based their calculations upon the assumption that the oil readily extractable from the flakes by shaking with petroleum ether represented oil from broken cells, while that obtained only upon prolonged extraction represented oil from unbroken cells Shchepkina estimated the proportion of broken cells upon the basis of the number of free aleurone grains in a portion of the sample

The mathematical analysis of data on the experimental solvent extraction of soybean flakes has led Osburn and Katz[18a] to suggest that, in flakes rolled to 0 008 to 0 021 inch in thickness, from 10% to 30% of the oil is contained in unruptured or partially ruptured cells

In any event, it appears that many oil cells remain intact after even the most careful reduction, and that the walls of these cells are made permeable to the oil only by the action of heat and moisture in the cooking operation However, the cell walls will be more readily acted upon by heat and moisture if the seed particles are small

Obviously the removal of oil by solvent extraction will be favored by disruption of the oil cells, to make the oil accessible to the solvent In the case of oil removal from material not directly accessible to the solvent, there is a direct relation between particle size and the speed and efficiency of extraction It has been shown that the controlling factor in the rate of solvent extraction of seed flakes is the internal resistance of the flakes to molecular diffusion of the solvent and the oil[19] With free circulation of the solvent, the rate at which oil diffuses from a flake is directly proportional to the surface area of the flake and inversely proportional to its thickness Thus the rate at which oil is extracted from a given weight of flakes is indirectly proportional to the square of the flake thickness Theoretically, for example, reducing the flake thickness from 0 012 to 0 006 inch should quadruple the rate at which the flakes can be reduced to a given

[16] W R Woolrich and E L Carpenter, *Mechanical Processing of Cottonseed* Engineering Expt Sta , Univ of Tennessee, Knoxville, 1935

[17] A M Goldovskii and M Podol'skaia, *Masloboino Zhirovoe Delo*, 10, No 4 (1934)

[18] O Shchepkina, *Masloboino Zhirovoe Delo*, 10, No 4 (1934)

[18a] J O Osburn and D L Katz, *Trans Am Inst Chem Engrs* 40, 511-531 (1944)

[19] D F Boucher, J C Brier, and J O Osburn *Trans Am Inst Chem Engrs* , 38, 967 993 (1942)

residual oil content. In practice, however, there are other factors to be considered, such as the mechanical strength of the flakes and the resistance offered by the flake mass to the flow of solvent. Consequently, for solvent extraction, seeds are not usually rolled to the least possible thickness The question of flake thickness in solvent extraction will be considered more fully in a later discussion of this process.

Hammer mills, attrition mills, and other devices are sometimes used for the preliminary reduction of large oil seeds, such as copra and palm or

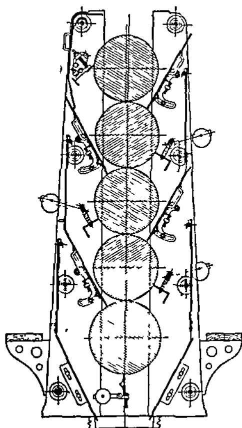


FIG. 42 —Five-high crushing rolls, cross section (Courtesy *The French Oil Mill Machinery Co*)

babassu kernels, but for the final reduction of oil seeds it is the almost invariable practice in the United States to use milling rolls. Rolls are generally considered to be more economical to operate than other types of mills. The thin flakes to which oil seeds are reduced by smooth rolls are more satisfactory for hydraulic pressing than the irregular shaped particles obtained by grinding. Flaking rolls are essential for preparing oil seeds for continuous solvent extraction, since no other form of mill is capable of forming particles which are thin enough to extract readily, yet large enough and coherent enough to form a mass through which the solvent will freely flow.

The roll assembly commonly used for the reduction of cottonseed, flax-

seed, and peanuts in the mills of the southern United States is a "five high" affair (Fig 42), consisting of a series of five rolls placed one above the other The seed is fed, by a feeding mechanism, between the two top rolls. It passes back and forth between adjoining pairs of rolls as it travels from the top to the bottom of the assembly, hence is actually rolled four times The assembly is so constructed that each roll supports the weight of all of the rolls above it, so that the seed particles are subjected to progressively increasing pressure as they pass from one pair of rolls to another Although the lower rolls are smooth, the top roll is commonly corrugated, to insure that the seed will be "nipped" as fast as they are fed to it A popular five high roll assembly consists of four upper rolls each 14 inches in diameter by 48 inches in width, and a bottom roll 16 inches by 48 inches in size, operating at a peripheral speed of about 630 feet per minute This unit has a rated capacity of 80 short tons of cottonseed or 300 bushels of linseed in 24 hours

Cottonseed are usually rolled to a thickness of between 0 005 and 0 008 inch The optimum yield of oil is said to be obtained with flakes of approximately the former thickness [16] The repeated passage of the material through the rolls results in considerable breaking up of the individual flakes, but this is not disadvantageous in the case of seed which is to be mechanically expressed Small oilseeds, such as flaxseed and sesame are usually rolled in preparation for expression

In the preparation of oil seeds for expression in expellers or screw presses, the production of thin particles is not so essential as for hydraulic pressing, since heat is generated and seed particles are broken up by the intense sheering stresses developed in the barrel of the expeller Soybeans which are to be processed in expellers are usually cracked into particles averaging 10 to 16 mesh in size, by corrugated cracking rolls, and are then expressed without rolling or further reduction Palm kernels, copra, peanuts, etc , are handled in expeller plants both with and without rolling Cottonseed are usually rolled before expression in expellers

The rolls used for flaking soybeans or other oil seeds for solvent extraction are somewhat different in design from those described above Since large, coherent flakes are desired for solvent extraction, the flaking operation must be carried out by a single passage of the whole or cracked seeds through the rolls A single pair of rolls, therefore, is provided, the rolls are mounted side by side rather than being superimposed, and are equipped with heavy springs to maintain the pressure of one roll against the other Since the clearance between rolls of this type is positively adjustable, flakes are produced of quite uniform thickness A novel design of rolls for preparing soybeans for solvent extraction has been patented by Ford and Boyer [20] This so called "horn angle" system employs a cylindrical roll which bears against the *inner* surface of a heavy cylinder rotating in the

[20] H Ford and R A Boyer, U S Pat 2 186 066 (1940)

same direction It has the advantage of having a smaller "angle of nip" than conventionally designed rolls of an equivalent size For this reason, a relatively small unit can handle large seeds A reasonably high moisture content is required in oil seeds which are to be formed into thin, coherent flakes Very dry seeds do not flake well

5 Heat Treatment of Oil-Bearing Materials

The heat treatments given oil bearing materials may be divided into two categories, according to whether they are alone productive of oil, or merely serve to facilitate the subsequent expression of oil by mechanical means The term "rendering" is generally applied to treatment designed to remove all or most of the oil from fatty animal tissues or other materials with a high ratio of oil to solid matter The heat treatment applied to oil seeds and similar materials prior to pressing is more commonly termed "cooking" Some methods of processing are a combination of rendering and cooking

In the case of either rendering or cooking, the principal object of the heat treatment is the same, *i e*, to coagulate the proteins in the walls of the fat containing cells and thus make the walls permeable to the flow of oil The flow of oil from the oil bearing material is also assisted by the lowered viscosity and surface tension of the oil at elevated temperatures Since oil containing materials are never completely dry, heat treatment is inevitably associated with various effects due to the presence of moisture, even when water is not added in the processing operation As a matter of fact, it is necessary for water to be present for the above mentioned protein coagulation to take place Anhydrous proteins do not readily coagulate or exhibit other evidences of heat denaturation In some cases water also assists in the displacement of oil from the surfaces of solid materials, through a superior physicochemical affinity for the latter

(a) *Dry Rendering*

"Dry" rendering is one of the simpler methods of oil extraction It is distinguished from "wet" rendering by the fact that the expulsion of oil is accompanied by dehydration of the fat and fatty tissues, so that the latter are essentially dry at the end of the operation The frying of bacon, to cite a familiar example, is essentially a dry rendering process

In its simplest form, dry rendering is carried out in an open kettle, which is equipped with a low pressure steam jacket and a low speed agitator designed to prevent the fatty tissues from adhering to the heated kettle walls The kettle may be of any convenient size, but will ordinarily hold several thousand pounds The well hashed stock is charged to the kettle without the addition of water, and is heated and stirred until the charge is substantially dry and at a temperature of 220° to 230°F The dried

residue of connective tissues, etc , or "cracklings," is strained and then pressed in a hydraulic or screw-type press

In the United States, leaf lard is almost invariably rendered by the "open kettle" method described above The quality of lard produced by this method is inclined to depend more upon the care exercised in handling the fatty stock than upon the details of the rendering operation In order to produce a fat low in free fatty acids, it is particularly important that the leaf fat be rendered soon after it is removed from the animal In some establishments it is customary to hang the fat in coolers for an overnight period before it is hashed and rendered It is preferable, however, to hash and render the warm fat immediately By this procedure it is possible to produce a lard with a free fatty acid content between 0 10% and 0 15% Lard rendered by the open kettle method has a distinctive "cooked" flavor which is preferred by many to the milder flavor of steam rendered lard Lard from other fat than leaf fat is occasionally rendered by this method, as are also tallow and other fats, especially in small establishments

Open kettle rendering is relatively slow and inefficient, and is not often used for the large-scale rendering of lard or other fats Manufacturers who prefer to render a large proportion of their fats by the dry method usually conduct the operation in closed tanks which during at least a portion of the rendering period are maintained under reduced pressure The application of vacuum greatly facilitates the removal of water from the charge, and protects the fat from oxidation Vacuum dry rendering is usually carried out in cylindrical, steam jacketed vessels, equipped with mechanical agitators and screens for separating the fats from the cracklings A typical batch dry rendering unit is described by Merkel[21] Continuous dry rendering systems have also been devised

Dry rendered fats contain a small amount of proteinaceous substances, which impart a distinctive flavor, and in some cases a somewhat dark color to the fat The color may be controlled to some extent by regulating the degree to which the charge is allowed to become dehydrated The coloring substances are inclined to enter the fat to a serious extent only if they have become excessively dehydrated They apparently exist in the fat in the form of a colloidal dispersion rather than a true solution, and can be partially precipitated and removed by hydration, by giving the fat a light alkali treatment, or even a water wash Because of the tendency of such substances to dissolve or disperse in dry-rendered fats, this method of rendering is usually confined to stock which consists substantially of fatty tissue, with little admixture of muscular tissue, etc Dry rendered fats, if prepared from fresh materials, are naturally lower in free fatty acid content than steam rendered fats, since they are not exposed to the hydrolyzing effect of long contact with steam or water at a high temperature

[21] A H Merkel, *Food Industries*, 8, 179-180 210 (1936)

(b) *Wet Rendering*

"Wet" rendering is carried out in the presence of a large amount of water, during the operation the separated fat rises to the top of the water and is skimmed off There are two varieties of wet rendering, *viz* , low temperature rendering, which is conducted at temperatures up to the *boiling point* of water, in open vessels, and high temperature or steam rendering, which is carried out under pressure, in closed vessels

Low temperature wet rendering is employed mainly where it is desired to produce a fat of very neutral flavor The apparatus used is simple, consisting of an open tank, equipped with a slow speed agitator and a jacket for steam at near atmospheric pressure The fatty stock is placed in the tank, water is added, and the contents are heated with gentle stirring, until the greater portion of the fat rises in a layer to the top of the kettle, after clarification with dry salt it may be drawn off The temperatures employed by different processors are somewhat variable, however the blandest fats are obtained by operating at the lowest practicable temperature, which may not be greatly in excess of the melting point of the fat, *e g* , 155°F in the case of oleo stock Rendering the stock at a low temperature does not result in a complete recovery of the fat, and it is customary to re render the residues, with other fatty stock, under steam pressure

The most important products of low temperature wet rendering are oleo stock and neutral lard

Low temperature wet rendering was formerly a process of great importance, before the techniques of producing neutral vegetable oils were well developed, and this was virtually the only method of obtaining fats suitable for margarine manufacture Lately the production of low temperature rendered fats has greatly declined The manufacture of oleo stock and oleo oil has decreased, and many establishments have discontinued the rendering of neutral lard altogether

Much the greater part of the animal fat produced in the United States is rendered by the steam process The lard produced by this method of rendering is known as "prime steam lard " In addition to lard, tallow and whale oil are also usually steam rendered

The apparatus used in packing houses in the United States consists of a vertical cylindrical steel autoclave or digester, with a cone bottom, designed for a steam pressure of 40 to 60 pounds per square inch and a correspondingly high temperature The vessel is filled about one third full of water and is then charged with the fatty material, and steam is admitted to boil the water and displace the air The vessel is then closed except for a small vent, and the injection of steam is continued until the operating temperature and pressure are attained, after which digestion is continued for a variable time, depending upon the temperature and the nature of the

charge. The usual digestion time amounts to 4 to 6 hours. Under the influence of the high temperature employed, the fatty materials in the digester disintegrate to some extent, and there is a very efficient separation of the fat, which rises to the top of the vessel, leaving a layer of "stick water" in the bottom. Pressure is then slowly relieved, and the fat–water interface is adjusted to the level of a draw off cock on the side of the vessel. The fat is drawn off and purified from traces of water and solid material by further settling and centrifuging or filtering.

The advantages of steam rendering are that an efficient recovery of fat is obtained in relatively simple equipment, and that it is adaptable to a wide variety of materials. There is little tendency for proteins, etc., to dissolve or disperse in the fat in the presence of water, hence the fatty stock may contain a large proportion of nonfatty tissue. Bony stock can be handled by this process, since it is effectively disintegrated by prolonged treatment with steam under an elevated pressure. Steam rendering is less rapid and less efficient from the standpoint of heat consumption than dry rendering, however, and a large amount of water must be evaporated in in order to recover the nonfatty residue in a concentrated form. The residue from most fatty material consists almost entirely of proteins.

Although most steam rendering systems are of the batch type, they may also be made continuous. A typical unit for the continuous digestion of whale blubber is described by Brocklesby.[14] This unit consists of feeding sluices, vertical preheating chambers, a horizontal rotary extractor, and a vertical settling tank, all interconnected by automatically operating valves. The hashed blubber is fed into the preheaters, where it is heated with open steam. From the preheaters it is discharged to the extractor, which consists of a horizontal drum, inside of which rotates a slightly smaller perforated drum or strainer. As the charge disintegrates, it gradually works through the strainer, and collects in the bottom of the fixed drum, from which it is pumped to the settling tank. After most of the water and solid material is removed from the fat by settling it is then centrifuged or filtered. Continuous rendering units are said to be gradually replacing other types for the extraction of whale oil.

(c) *Cooking of Oil Seeds*

It is universally recognized that oil seeds yield up their oil more readily after cooking, but a complete explanation of why this is so is at present lacking. It is certain that the changes brought about by cooking are complex and that they are both chemical and physicochemical in nature.

The oil droplets in a cottonseed or similar oil seed are almost ultramicroscopic in size, and are distributed throughout the seed. One effect of cooking is to cause these very small droplets to coalesce into drops large enough to flow from the seed. An undoubtedly important factor in this

phase of the process is the heat denaturation of proteins and similar substances. Before the proteins become coagulated, through denaturation, the oil droplets are virtually in the form of an emulsion. Coagulation causes the emulsion to break, after which there remains only the problem of separating gross droplets of oil from the solid material in the seed. Since the surface of the seed particles is highly extended, surface activity figures prominently in the displacement of the oil. Cooking, in turn, has a profound influence upon the surface activity of the material. The objects of the cooking process may therefore be summarized as follows: (*a*) to coagulate the proteins in the seed, to permit coalescence of oil droplets and to make the seed permeable to the flow of oil, and (*b*) to decrease the affinity of the oil for the solid surfaces of the seed, in order that the best possible yield of oil may be obtained when the seed are subsequently pressed.

One factor which obviously affects the affinity between the seed and the oil, and which is amenable to control in the cooking operation, is the moisture content of the seed. Very dry seeds cannot be efficiently freed of their oil. However, it is impossible to say just how moisture inhibits wetting between the seed and the oil. It may be that the cooking process produces a film of adsorbed liquid water on the seed surfaces, which displaces the oil. On the other hand, the water may be in a more nearly "bound" state, and its presence in the seed in this condition may serve to make the seed surface relatively lipophobic. The optimum moisture of cooked seed varies widely, according to the variety of the seed and the method to be used for expression. Thus, for example, the preferred moisture content for soybeans which are to be expressed in expellers is but 2–4%. On the other hand, cottonseed and sunflowerseed are processed in Russian mills, by the Skipin process,[22] at moisture contents as high as 20–21%. The function of moisture in displacing oil from oil seeds has been particularly emphasized by Goldovskii and other Russian writers.[23]

There are many substances in oil seeds which are surface active, such as phosphatides and free fatty acids, and the degree to which these are present or become active during cooking doubtless influences the tendency of the seed to adsorb and retain oil. It is generally observed that damaged oil seeds give lower yields of oil than undamaged seeds of equivalent oil content. The tendency of damaged seed to retain oil tenaciously is probably due to their high content of free fatty acids or other surface active agents.

In addition to its effect upon the yield of oil, the method of cooking also determines to a considerable degree the quality of both the oil and the oil

[22] A. I. Skipin, *Trudy VNIIZh*, 40 pp. (Sept., 1935).

[23] A. M. Goldovskii, *Fettchem. Umschau* **43**, 21–26, 57–61, 84 (1936); *Trudy NIRMMI*, No. 1, 64 pp. (1933). A. M. Goldovskii and M. Liubarskaia, *Masloboino Zhirovoe Delo*, **11**, 586–587 (1935).

cake Cooking is particularly important in its relation to the refining loss of the oil A large part of the oil lost in caustic refining consists of neutral oil which is emulsified in the foots Certain surface active agents naturally present in the oil favor this emulsification others appear to inhibit it [24,25] The relative proportions of the two classes of substances in the oil depend to a great extent upon the operation of the cooker There is little published information relative to the identity of the surface active agents in crude oils but it would appear that the substances responsible for high refining losses are generally phosphatides or related substances The presence of gossypol in cottonseed oil is known to contribute to the production of hard foots and a low refining loss [5] Little information is available as to specific methods followed by different mill operators to obtain oil with a minimum refining loss but the object in general is to maintain the phosphatides in such a form as to prevent their excessive solution in the oil The refining losses of both cottonseed oil and peanut oil may be increased greatly by improper cooking of the seeds The relation between cooking methods for cottonseed and the refining loss of the expressed oil is discussed by Thornton,[6] who recommends the shortest possible cooking period at the lowest practicable temperature with the seed being brought to cooking temperature as rapidly as possible Thornton also recommends that any water added during cooking be added hot to the well heated seeds Some oils such as soybean oil are customarily hydrated with water or steam and then centrifuged for the removal of phosphatides after extraction or expression, but this treatment has not generally proved economically feasible in the case of other oils such as cottonseed or peanut oil

It is undesirable for the seeds to darken unduly in the cooker as light colored oilcake is generally preferred over dark cake There is of course extensive denaturation of proteins in cooking which may or may not be advantageous For feeding purposes a well cooked cake is desired Cooking *has the effect of detoxifying the gossypol present in cottonseed* and appears to render the proteins of other oil seed more readily assimilable by the animals to which they are fed Solvent extracted soybean meal is customarily cooked or toasted before it is shipped from the mill On the other hand cooking is generally undesirable for seed residues which are to be put to industrial uses such as the manufacture of protein coatings sizes adhesives plastics or fibers

The cooking of oil seeds for hydraulic pressing is usually carried out in stack cookers These (Fig 43 page 467) consist of a series of three to six closed superimposed cylindrical steel pans each 2 to 7 feet in diameter and 1 5 to 2 5 feet high Each pan is independently jacketed for steam

[24] J J Ganucheau and E L D Aquin *Oil & Soap* **10** 49–50 (1933)
[25] H D Royce and F A Lindsey *Ind Eng Chem* **25** 1047 1050 (1933)
[26] M K Thornton Jr *Oil & Soap* **14** 151–152 (1937)

heating on both sides and bottom, and is equipped with a sweep type stirrer mounted close to the bottom, and operated by a common shaft extending through the entire series of pans There is an automatically operated gate in the bottom of each pan except the last, for discharging the contents to the pan below, the last or bottommost pan feeds into a cake former The top pan is provided with spray jets, for the addition of moisture to the seed, and each of the lower pans is provided with an exhaust pipe and fan, for the removal of moisture Thus it is possible to control the moisture of the cooking seed, not only with respect to their final moisture content, but also at each stage of the operation

In operation, the rolled seed are delivered at a constant rate to the top pan, by means of a conveyor After a predetermined period of cooking in each pan, each charge of seed is automatically dropped to the previously emptied pan below, so that there is a continuous progression of seed downward through the cooker The gates which govern the flow of meats from one pan to another may be motor operated, or as is more usually the case, they may be opened and closed automatically by a mechanism which engages the seed at a specific level in each pan In the latter case, the time that the seed charge remains in each pan is determined by the seed levels for which the pans are set An 85 inch, five high cooker, which is a common size, has a rated capacity of 130 tons of cottonseed (calculated upon the basis of the whole seed) per 24 hours

Steam pressure on the upper stacks of a stack cooker is usually maintained at a relatively high value, e g, 60 to 70 pounds per square inch, in order to provide quick heating On the lower stacks it is usually reduced somewhat, since here it is only necessary to maintain the heated seed at cooking temperature Cottonseed are usually kept in the cooker for 80 to 90 minutes, and are brought out at a temperature of 225° to 235°F Peanuts are often cooked for a somewhat shorter period Oil seed are usually moistened before cooking, or during the early stages of cooking, unless they are initially fairly high in moisture, and their moisture content is then reduced in the cooker Thus Woolrich and Carpenter[16] recommend an initial moisture content of 12% and a final moisture content of 8–9% in the cooking of cottonseed

A pressure type cooker has recently been introduced in the United States for the cooking of cottonseed[27,28] and has found considerable favor with some mill operators This apparatus consists of a horizontal steam jacketed cooker, provided with an unheated, vertical holding tank above, and another vertical receiving tank below The cooker is built to withstand moderate pressure, and is provided with a steam line for the direct injection of steam Its interior is accurately machined to a cylindrical

[27] J Leahy, *Southern Power and Ind*, 57, No 10, 37–44 (1939)
[28] R W. Morton, *Mech Eng*, 62, 731 735 (1940)

form, and is provided with a stirrer which operates with a very close clea ance (*ca* $\frac{1}{32}$ in) between the stirrer blades and the cylinder walls. T rolled seed are dropped in batches from the holding tank into the cool and thence into the receiving tank, which discharges to the cake form Each batch is cooked for 10-20 minutes at about 260°F Pressure cooki not only materially shortens the cooking cycle, but is also claimed to i prove the yield and quality of the oil

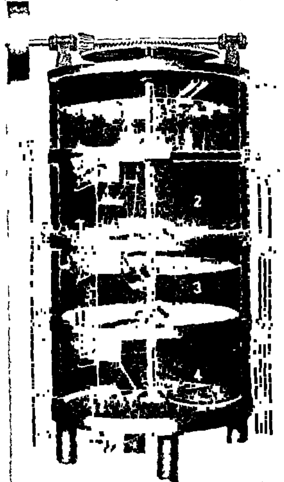


FIG 43 —Four—high stack cooker (Courtesy *The French Oil Mill Machinery C*

A novel cooking method developed by Skipin[22] is said to be in comm use in Russian oil mills This method depends upon the discovery th at a critical temperature, and at a likewise critical and somewhat hi moisture content, oil seeds such as cotton, sunflower and sesame can made to yield 50% or more of their oil in the cooking pan The succe of the method seems to depend upon the selection of conditions under whi there is an extremely selective wetting of the solid seed surfaces by wat

in preference to oil Use of the Skipin process does not improve the recovery of oil from the seed, but it is said to increase the capacity of oil mills in which it is used by as much as 50–100%

In the Skipin process the preliminary separation of oil is obtained in a "forepan," which is similar in construction to a single pan or stack of an ordinary large stack cooker, except that it is equipped with a perforated false bottom The rolled seed are charged to the forepan, and a sufficient quantity of water is added in the form of a spray to bring the water content of the seed to the optimum level The moistened mass is then quickly heated with superheated steam to the proper temperature, the heating operation requiring 5 to 6 minutes It is then maintained at this temperature and slowly stirred, whereupon about half of the oil separates and is drained off through the perforated bottom During the operation, the residue agglomerates into sizable, plastic lumps Approximately 30 minutes is allowed for drainage of the oil After drainage is completed, the somewhat sticky residual lumps are transferred to a "companion pan," and dried until they have lost 2–2 5% of moisture and have become friable They are then transferred to stack cookers and cooked, dried and pressed in the usual manner It is stated that in the processing of sunflower seed it has been possible by means of the Skipin method to increase the turnovers of Anglo American presses from 2 0 to 2 50 and in some cases 2 75 per hour, without increasing the oil content of the press cake Cottonseed oil extracted in the first stage of the Skipin process is said to have an extremely low refining loss, due to its high content of gossypol [29]

The temperatures and moisture contents recommended by Skipin[29] for various oil seeds are listed in Table 138

Another distinctive Russian method of oil seed extraction is that of Iljin,[30] which is designed to effect improvements in the yield of oil rather than mill capacity The Iljin method is also founded upon the principle of moistening of the seed in order to accomplish displacement of the oil It involves a first pressing of the seed under more or less conventional conditions, followed by a re-pressing of the cake after it has been broken up and moistened with live steam

The heat treatment of oil seeds for continuous pressing, by means of screw presses or expellers, is somewhat different from that given seeds which are to be hydraulic pressed Seed which are to be expeller pressed must be not only cooked, but also dried to a considerable extent, since continuous presses of this type operate satisfactorily only on material of rather low low moisture content, usually between 2% and 5% Cracked soybeans which have been prepared for expeller pressing are usually dried to 2% to 3% moisture by passage through continuous rotary steam heated dryers,

[29] A I Skipin and M Sokolova *Masloboino Zhirovoe Delo*, **10**, No 8 4–11 (1934)

[30] See R Heublyum and H Japhe, Footnote 1 p 441

equipped with exhaust fans and dust collectors In the dryers the beans are brought to a temperature in the neighborhood of 270°F They are delivered to the expellers at the same temperature, but in order to allow time for protein denaturation and for equilibrium conditions of heat and moisture to be attained throughout the seed particles, they are subjected to an intervening "tempering" period, in steam heated troughs provided with screw conveyors, which are integral with the expellers or screw presses The seed experiences a further heat treatment within the expeller barrel, from heat developed by frictional resistance to their passage The maximum temperature attained by the seed mass may be well in excess of 300°F Peanuts are not as yet processed in continuous presses on anything but a very small scale, at least in the United States but presumably they would require a heat treatment similar to that given soybeans Copra and babassu kernels are dried and tempered similarly to soybeans

TABLE 138
SEPARATION OF OIL FROM OIL SEEDS BY THE SKIPIN METHOD
OPERATING CONDITIONS

Seed	Percentage moisture at which oil separated in forepan	Percentage hulls in the meal	Temperature at which oil begins to separate in forepan °C	Final temperature at which oil separates in forepan °C
Sunflower	13 5–21 0	7 8	60	85
Castor whole	14 5–19 0	24–23	60	82
Castor, hulled	11 5–16 0	2–3	60	82
Cotton	14 5–20 0	5 6	70	72
Hemp, whole	15–20	—	70	72
Cedar nut	16–20	2 3	35	37
Peanut	16–20	2–3	35	37
Sesame	16–20	1 2	35	37

In the processing of cottonseed and flax seed the rotary dryers are omitted, and the cooking and drying operation is carried out in a series of continuous, steam jacketed, horizontal cookers designed to operate under slight steam pressure, which are built directly on the expeller The seed are rolled before being delivered to the cookers, and are fed to the expeller at a somewhat lower temperature and at a higher moisture content than soybeans

6 Mechanical Expression of Oil

(a) *Batch Pressing*

The oldest and most common method of oil extraction comprises the application of pressure to batches of the oil bearing material confined in bags, cloths, cages, or other suitable devices

Levers, wedges screws, etc have been used as a means of applying pressure in the more primitive styles of presses, but modern presses are almost

invariably actuated by a hydraulic system Thus the term "hydraulic pressing" is often used in reference to batch pressing in general There is a limited use of mechanically operated presses for special purposes where a relatively light pressure only is required as for example in the pressing of partially solidified oleo stock or lard to yield oleo oil or lard oil

Batch presses may be divided into two main classes consisting of the "open" type which requires the oily material to be confined in press cloths and the "closed" type which dispenses with press cloths, and confines the material in some species of cage Open type presses may be subdivided into plate presses and box presses and closed type presses may be classified as pot presses or cage presses

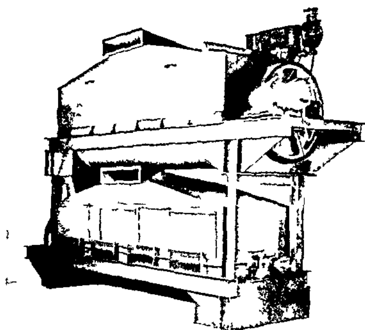


FIG 44 —Soybean drier (Courtesy *The V D Anderson Co*)

The frame of an open or Anglo American press (Fig 45) consists of four heavy, vertical steel columns fastened at the top and bottom to heavy end blocks Within the open cage formed by the columns and suspended from the top of the press are a series of horizontal steel plates These plates closely fill the space enclosed by the columns They are equally spaced at intervals of about 3 to 5 inches and are suspended one from the other by linkages which permit the entire assembly to become compressed in the pressing operation Below the plate assembly and attached to a ram operated from below, is a heavier bottom plate The material to be pressed is formed into rectangular cakes which are placed between the various suspended plates Raising the ram compresses the series of cakes and causes

the oil to fall into a drip pan resting upon the bottom block The stress created by the application of pressure is directed against the top block and is translated into longitudinal stress upon the four columns

In ordinary plate presses, the oil seed flakes are completely wrapped in press cloths and placed between the plates without the use of accessory devices to restrain the cake mass as it is pressed The surfaces of the plates, however, are usually either corrugated or covered with hair mats, to assist in the drainage of the oil and to overcome cake creepage Box presses are provided with a special boxlike arrangement (Fig 46) which encloses the cake on its two long sides, and simplifies the wrapping of the cake The complete press box includes a corrugated drainage rack a perforated and corrugated steel drainage mat which rests upon the drainage rack and underneath the cake, and steel "angles" which project from the underside of each plate to form the sides of the box enclosing the cake below With this arrangement, it is only necessary for the press cloth to enclose the cake on the top bottom, and ends Thus folding of the press cloth in two directions is avoided, and very heavy, durable cloths may be used Standard size press boxes are about 2 inches deep, and are 35 inches long 14 inches wide at the back, and 14⅜ inches wide at the front, being slightly widened from back to front to facilitate insertion and removal of the cake Presses are usually constructed with either 15 or 16 boxes Plate presses of an equivalent size have 24 plates, and hence have a greater capacity than box presses

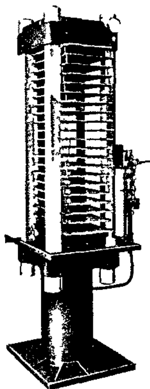


FIG 45 —A Plate press (Courtesy *The French Oil Mill Machinery Co*)

Presses similar to those described above are generally provided with a 16 inch ram operating at a pressure of 4000 to 4500 pounds per square inch, hence the pressure on the cake is between 1650 and 1850 pounds per square inch It is important to build up pressure upon the cakes gradually In order to conduct the initial stage of compression more rapidly than the later stages, the hydraulic system operating the presses is provided with automatic valves which deliver oil at 500 pounds' pressure to the ram until an equivalent pressure is built up on the cake, and thereafter deliver the maximum pressure of about 4000 pounds The time allowed for drainage of the oil after the maximum pressure is reached is somewhat variable

amongst different mill operators However, a typical press cycle is as follows for charging the press 2 minutes, for attaining maximum pressure 6 minutes, drainage time, 26 minutes, for discharging the press 2 minutes total 36 minutes The capacity of a 15 box press operated under these conditions is approximately 11 short tons of whole cottonseed or whole peanuts per 24 hours

An essential accessory to the operation of either plate or box presses is a cake former for automatically delivering a proper quantity of flakes from the cooker and forming the flakes into a cake of the proper size and shape within the press cloth Cake formers are designed to press the flakes into a coherent mass without the application of sufficient pressure to start the oil from them They are hydraulically operated Mechanically operated cake strippers are also provided for removing the somewhat adherent press

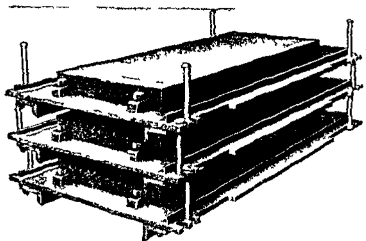


FIG 46 —Press box assembly for use in box press (Courtesy *The French Oil Mill Machinery Co*)

cloths from the spent press cake Charging and discharging the presses is carried out entirely by hand, however An operator is also required for both the cake former and the cake stripper as neither is fully automatic

The edges of the cake coming from an open type press are soft and higher in oil content than the remainder of the cake Consequently, it is the usual practice to slice off or beat off these edges in a mechanical cake trimmer and rework the trimmings through the presses

Plate presses are usually preferred for flaxseed whereas box presses are standard equipment in cottonseed or peanut mills The press cloths used with box presses are woven from either camels hair or human hair A wide variety of materials are used for the cloths used in plate presses including cotton, wool, hair etc

Cage presses (Figs 47 and 48) confine the oil containing materials within a strong perforated steel cage during the pressing operation and thus

largely dispense with the use of press cloths They may be operated at higher pressures than are practicable with open presses They are particularly suitable for the expression of copra palm kernels and other oil seeds which are high in oil content and low in fiber and hence are inclined to flow and burst the press cloths of open presses Castor beans or other seeds which it is desired to process without heat treatment can be pressed satisfactorily only in presses of this type as very high pressures are required to extract the oil efficiently from cold seeds They are desirable for use by

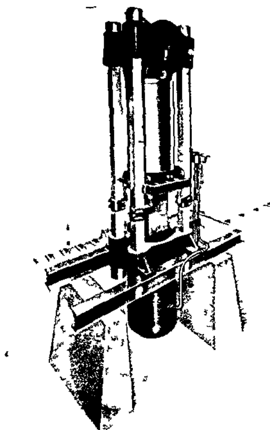


FIG 47 Cage press (Courtesy *The French Oil Mill Machinery Co*)

mills which process a large number of varieties of oil seeds as they can be used on practically any oil seed or other oily material

Cages for this type of press are built in both round and square forms They are usually made up from a number of closely spaced steel bars or slotted steel plates supported inside a heavy frame or ringed with heavy steel bands The channels through which the oil escapes are increased in size from the interior of the cage outward to minimize any tendency for them to become clogged with solid particles The cages are operated in a vertical position in a frame similar to that of the Anglo American press

Oil is expressed from the charge by forcing a closely fitting head up into the cage from below by means of a hydraulically operated ram. The upper end of the cage may be closed solidly, in which case pressure is applied only to one end of the charge, or the cage may float between the lower ram and an opposed head entering from above. In the latter case, pressure is applied to both ends of the seed mass. Cage presses are designed to attain pressures of 6000 pounds per square inch, or more.

Since there is a marked tendency for the oil flow in the compressed cake to be longitudinal rather than radial, the cage cannot be packed solidly with the oil seed, but must be charged with layers of seed, which are separated by drainage plates and press cloths. Auxiliary equipment is required

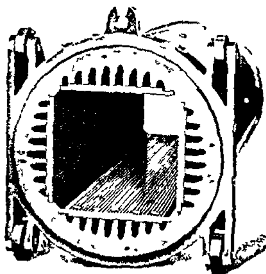


Fig. 48.—Square cage from cage press. (Courtesy *The French Oil Mill Machinery Co.*)

for filling the cages and discharging the cake. This, and the rather elaborate and heavy design of the cages, makes the initial cost of this type of pressing equipment relatively high. In large installations the cages are usually made removable from the presses, and filling and discharging presses are provided, in addition to a number of finishing presses. A cage carriage is provided for transferring the havy cages from one press to another.

The pot press (Fig. 49) is a special form of cage press used for the extraction of cocoa butter or other fats which are solid at ordinary room temperature. In this press the cage is replaced by a series of short, superimposed, steam heated cylinder sections or "pots." The walls of the pots are

solid and drainage takes place through perforated plates and filter mats in the bottom of each section Pot presses are usually designed for pressures intermediate between those employed in open presses and cage presses although they can be built for virtually any desired pressure The advantages of pot presses are that they can be heated and that they can handle very soft nonfibrous material such as fruit pulp at high pressures without forcing large quantities of solid material into the oil Their capacity is

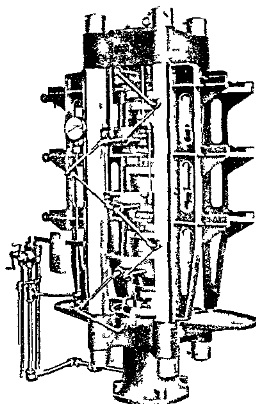


FIG 49 —Pot press (Courtesy *The French Oil Mill Machinery Co*)

small however in relation to their size and cost and they require more hand labor to operate than other types of presses

Some oil seeds of high oil content such as copra are difficult to express satisfactorily in batch equipment by a single pressing In some places it is customary to break up the oil cake derived from the first pressing and subject it to a second pressing with or without intervening moisture or heat treatment for the recovery of residual oil Such practice of course requires a double reduction of the seed and is also inclined to yield an oil of inferior quality from the second pressing In American practice the

double pressing of oil seed is generally considered an obsolete method Oil seeds which cannot be reduced to a low oil content by a single pressing in hydraulic presses are preferably processed in continuous screw presses or expellers

Koo,[31] as a result of laboratory pressings of decorticated, ground, and cooked soybeans cottonseed, rapeseed, peanuts, sesame seed, tung nuts and castor beans, has advanced the following general equation for oil expression by hydraulic pressing

$$W = CW_0 \frac{\sqrt{P}\,\sqrt[6]{\theta}}{\nu^z}$$

where W is the oil yield in terms of weight per cent on a dry basis C is a constant characteristic of each kind of oil seed W_0 is the oil content of the seed expressed on a dry basis P is the pressure, θ is the pressing time, ν is the kinematic viscosity of the oil at the pressing temperature, and z is an exponent which has the value of $\frac{1}{2}$ for soybeans and cottonseed $\frac{1}{3}$ for rapeseed peanuts and tung nuts and $\frac{1}{6}$ for sesame seed and castor seed The values found for C the press constant were as follows for soybeans 0 0045 for cottonseed 0 00535, for rapeseed, 0 00583, for peanuts, 0 00751, for sesame seed 0 00835 for tung nuts, 0 00907, and for castor beans, 0 00921

(b) *Continuous Pressing*

Expellers or screw presses are used to the almost complete exclusion of hydraulic presses for the mechanical extraction of soybean oil in the United States and are also extensively used throughout the world for the expression of copra palm kernels peanuts cottonseed flaxseed, and almost every other variety of oil seed

Presses of this type are continuous and in most respects automatic in operation They effect a large saving in common labor over hydraulic systems and completely eliminate the need for press cloth They are adaptable to a wide variety of materials, and in most cases, they produce a slightly higher yield of oil than hydraulic presses Their principal disadvantages are that their power requirements are relatively high, they require fairly well skilled labor for both operation and maintenance and they are not well adapted to intermittent operation

The expeller is essentially a continuous cage press, in which pressure is developed by a continuously rotating worm shaft, rather than an intermittently operated ram An extremely high pressure, of the order of 15,000 to 20 000 pounds per square inch is built up in the cage or 'barrel,' through the action of the worm working against an adjustable pressure orifice or choke, which constricts the discharge of cake from the end of the

[31] E C Koo *Ind Eng Chem* **34**, 342-345 (1942)

barrel The interiors of the barrels of these machines are made up of flat steel bars which are set edgewise around the periphery of the barrel and are held in place by a heavy cradle type cage The openings between the barrel bars through which the oil must flow can be adjusted by changing the thickness of spacers placed between the bars

Installations of continuous presses for oil seeds in the United States are practically confined to two makes which are similar in principle but slightly different in construction One of these (Fig 50) employs a vertical barrel which receives the seed presses out approximately half the oil and then passes the partially expressed seed to a larger horizontal barrel in

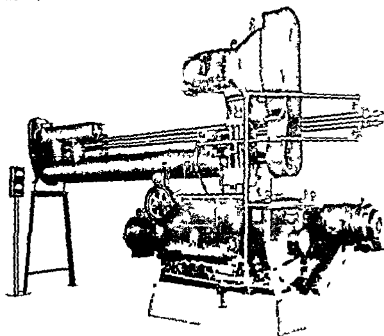


Fig 50—Modern expeller for soybeans (Courtesy *The V D Anderson Co*)

which additional oil is expressed at a higher pressure The worms are powered by a 40 h p electric gear reduced motor The barrel is cooled while the machine is in operation by passing the expressed oil through a water–oil heat exchanger and then flushing the cooled oil over the exterior of the barrel The main worm shaft may also be water cooled if this is desired A duplex model is made by the same manufacturer in which the vertical worm is independently powered by a motor whose speed varies with the load imposed upon it This arrangement insures a proper coordination of pressing action in the two barrels under wide variations in the character of the seed being pressed and hence is advantageous if the unit is to be used on a variety of oil seeds Smaller models are also manufactured in which the vertical barrel and worm are omitted

The other make of screw press has but a single barrel, but the worm is split into two sections, which revolve at different speeds The first portion of the worm revolves more rapidly than the latter portion and has deeper flights Thus its action corresponds to that of the vertical worm of the machine described above It receives the seed, presses out a portion of the oil at relatively low pressure, and feeds the seed mass to the more slowly revolving screw in the fore part of the barrel, which finishes the pressing operation at an increased pressure In this machine, cooling of the barrel is obtained by circulation of water through channels in the cage members

The oil expressed by expellers invariably contains a greater proportion of foots or solid material than hydraulic pressed oil For the removal of this material, expeller plants are equipped with screening and draining devices which remove the greater portion and return it to the feed of the machines The oil is usually given a final filtration in a filter press, to remove small particles which are not recovered by screening The removal of meal or foots from the oil is highly necessary, as such material increases the refining loss of the oil out of proportion to its actual amount

The larger size expellers and screw presses have a 24 hour capacity of 18 to 22 tons of soybeans and 22 to 24 tons of cottonseed (whole seed basis) Their capacities on other oil seeds are copra or babassu kernels 18 to 20 tons, flaxseed, about 15 tons

Freshly pressed soybean expeller cake is both very dry and very hot It is usually sprinkled with sufficient water as it leaves the expeller to reduce its temperature and increase its moisture content from about 2% to 10–12% On the basis of a 10% moisture content, the oil content of soy bean cake is usually between 4 5% and 5% In well operated expeller plants, 43% protein cottonseed cake can consistently be produced with an oil content of 4% or less Flaxseed cake produced by expellers usually has an oil content of less than 4%

Expellers and screw presses of the same design as those used for oil seeds are sometimes used for pressing whale or seal flesh or fish and for processing meat scraps, but these materials are more commonly handled in screw presses which are specially designed for the purpose These are generally of lighter construction than the machines built for oil seed extraction and are operated under lower presses A modern unit for the recovery of oil from sardines or similar fish, which employs a screw press in connection with a continuous pressure cooker and meal drier is described by Brocklesby [14] The extract from such materials consists of a mixture of water and oil, with a small amount of solid matter The oil must of course be further separated by settling centrifuging filtering, etc

(c) *Centrifugal Expression*

Centrifugation is used in isolated cases, either alone or as an adjunct to mechanical expression, for the extraction of oil from a variety of fatty mate

rials, but the only material for which it is a standard method of extraction is palm fruit The centrifugal expression of palm oil will be discussed in some detail in a later part of this chapter The centrifuges which are suitable for oil extraction are of the basket type, equipped with a removable, perforated cage, and do not usually have a capacity in excess of about 500 pounds of material

7 Solvent Extraction of Oil

(a) *Applications*

In the processing of any oil material with a fairly high solids content, the greatest yield of oil can be realized only by extraction with solvents However, solvent extraction is much more advantageous in the case of some materials than others At the present time this process finds its most important application in the recovery of oil from soybeans

The large scale extraction of soybeans originated in Germany, and has been used there and in other European countries almost to the exclusion of other methods of processing In the United States solvent extraction of soybeans is less generally practiced although it was estimated[32] that in 1939, 20 2% of a total of 1,712 152 tons was processed by this method, as compared with 74 4% processed in expellers and 5 4% handled in hydraulic mills The solvent extraction process, in its relation to both technical and economic factors has recently been discussed in some detail by Goss,[32] who points out the following circumstances as having encouraged its development in Europe and hindered its general adoption in the United States (*a*) The soybean is uniquely adaptable to solvent extraction (*b*) The soybean has only recently become a major American oil seed crop (since about 1935), whereas Manchurian soybeans became plentifully available in Germany a good many years ago (*c*) Solvent extraction has been commercially successful only in relatively large installations, the fact that European oil seeds are largely imported has favored the erection of large processing establishments whereas the industry in the United States is for the most part decentralized (*d*) Because of general domestic deficiencies in oil production, there has been a greater need in European countries for attaining the highest possible yield of oil

The total capacity of all continuous solvent extraction plants in the United States, in comparison with the total world capacity of such plants (as of 1941) was estimated by Goss to be as follows U S capacity, 1,555 short tons per 24 hours, world capacity, 6 475 short tons per 24 hours

Solvent extraction is relatively more advantageous in the processing of soybeans than other oil seeds because of the low oil content of this particular seed The oil content to which oilcake can be reduced by mechanical expression is approximately the same for all oil seeds, *i e*, about 4–5%

[32] W H Goss *Chem & Met Eng*, 48, No 4 80–84 (1941)

Consequently, the oil unrecoverable by mechanical expression, in terms of percentage of the total oil, increases progressively as the oil content of the seed decreases Comparative yields of oil from representative seeds of low, medium, and high oil content by the two methods of processing, are shown approximately in Table 139 It will be seen that the substitution of solvent extraction for pressing methods may increase the yield of oil from soybeans by 20%, whereas in the processing of cottonseed the increase may be only about 7%, and in the case of peanuts it may be but 3%

TABLE 139

COMPARISON OF SOLVENT EXTRACTION AND THE MOST EFFICIENT MECHANICAL EXPRESSION AS APPLIED TO OIL SEEDS OF LOW MEDIUM AND HIGH OIL CONTENT

Oilseed *Oil content*		*Soybeans* *Low*	*Cottonseed* *Medium*	*Peanuts* *High*
Composition of flaked seed lbs /100 lbs seed				
Oil		18 6	32 5	50 0
Solids		69 0	60 0	44 0
Moisture		12 4	7 5	6 0
Yields from processing, lbs /100 lbs flaked seeds				
Mechanical expression				
Oil	Oil	15 0	29 8	48 0
Cake or meal	Oil	3 6	2 7	2 0
	Solids	*69 0*	*60 0*	*44 0*
	Moisture	9 0	5 0	4 0
Per cent oil in cake		4 4	4 1	4 0
Per cent total oil recovered		80 6	91 7	96 0
Solvent extraction				
Oil	Oil	18 0	32 0	49 65
Cake or meal	Oil	0 6	0 5	0 35
	Solids	69 0	60 0	44 0
	Moisture	*9 0*	*5 0*	*4 0*
Per cent oil in cake		0 76	0 76	0 72
Per cent total oil recovered		96 7	98 5	99 3
[illegible]				
		15 0	29 8	48 0
		18 0	32 0	49 65
		3 0	2 2	1 65
		20 0	7 4	3 4

In some cases the application of solvent extraction to specific oil seeds is limited by mechanical considerations The most efficient extraction is obtained only in continuous counter current systems, in which the solvent and the seeds make contact with each other in streams moving continuously in opposite directions Most of these systems can be operated satisfactorily only if the seed flakes substantially retain their original form during extraction If the flakes are inclined to disintegrate under the influence of the solvent, the fine particles will not only be difficult to separate from

the miscella, but will also impede its uniform circulation through the seed mass. Soybeans can be rolled to thin, coherent flakes which are excellently adapted to solvent extraction. Whole cottonseed meats also form flakes which are suitable for extraction; such meats have been satisfactorily processed in experimental lots in soybean extractors of the Bollman type. Peanuts, however, disintegrate to a virtual powder in extraction, and hence can probably not be handled except in special types of equipment, such as that designed by Fauth.[33]

It is possible, by extracting the hydraulic- or expeller pressed oil cake, to recover almost all the oil from oil seeds which cannot be satisfactorily extracted in their original form. The solvent extraction of mechanical press residues is not generally practiced in the United States, except in the case of castor bean pomace, but is common in Europe. The oil obtained from the cake is invariably inferior in quality to that expressed from the seeds, since it contains a disproportionate amount of the pigments, phosphatides, and other nonoil constituents of the seed.

In addition to its use in processing oil seeds of low oil content, solvent extraction may be peculiarly advantageous in the recovery of oils which are scarce or expensive. Castor bean residues from hydraulic cold pressing are customarily solvent extracted in batch extractors. Solvent extraction may also be resorted to in order to obtain a fat free residue, or a residue in which proteins are not heat denatured, rather than for the primary purpose of improving the yield of oil. Thus, for example, cocoa beans are solvent extracted in order to produce a residue which may serve as a source of theobromine. Solvent-extracted meal is preferred for the manufacture of protein adhesives, fibers, or plastics, since there is much less denaturation of the protein in this meal than in that obtained by cooking and mechanical pressing.

The recovery of fat from garbage is often carried out by means of solvent extraction, since the low fat content of this material makes other methods of recovery difficult. Garbage is extracted in batch equipment of special design.

A rather elaborate cost analysis of solvent extraction, in comparison with mechanical expression, is presented in a recent article by Bilbe.[34] The economics of solvent extraction by the Hildebrandt system have been discussed in some detail by Meyerweissflog.[35]

(b) *Principles*

The laboratory extraction of an oil material in an ordinary Butt extraction tube is an example of solvent extraction in its simplest form. In this method of extraction, the pure solvent is delivered continuously to the

[33] P. L. Fauth, U. S. Pat. 2,253,696 (1941).
[34] C. W. Bilbe, *Mech. Eng.* **63**, 357-360 (1941).
[35] W. E. Meyerweissflog, *Oil & Soap*, **14**, 10-14 (1937).

top of the mass of material to be extracted, and is percolated through the mass by gravity, until the removal of oil is substantially complete While this method is effective in the laboratory, it is highly inefficient Complete extraction can be accomplished only by the use of a large volume of solvent relative to the volume of oil extracted This solvent must eventually be recovered from the oil Even in the most efficient extraction plants, charges for steam and water for solvent recovery constitute a substantial part of the operating costs,[34] and if the ratio of solvent to oil is high, such charges may easily become prohibitive A prime object in modern solvent extraction practice is to reduce the solvent content of the final miscella or oil-solvent mixture to the lowest possible figure In the best continuous extraction plants the solvent-oil ratio may be as low as 3 to 1, whereas by simple percolation an equivalent extraction could hardly be accomplished with several times as much solvent

Some improvement in efficiency is obtained if the continuous percolation of fresh solvent, as described above, is replaced by prolonged treatment of the oil seeds or other material with successive portions of solvent Each portion is recirculated through the material being extracted until equilibrium or near equilibrium is established between the oil content of the solid material and that of the solvent, *i e*, until the free miscella is as rich in oil as the miscella absorbed within the solid particles When this condition is attained, the free miscella is drained off, a fresh batch of solvent is brought into the system, and the operation is repeated Extraction is thus continued, in successive cycles of recirculation and drainage, until the oil content of the material is reduced to the value desired

While batch extraction by means of percolation is satisfactory for some materials, it is not generally adaptable to the large scale processing of oil seeds It is virtually impossible to charge large extraction chambers with oil seed flakes without uneven compacting of the material and consequent channelling and incomplete extraction Hence batch extractors for oil seeds are generally provided with some means of mechanically mixing the solvent and the seed particles However, from the standpoint of efficiency in maintaining a low solvent-oil ratio it is immaterial whether the solvent and the oil seeds are brought into equilibrium with respect to oil content by circulating the solvent through the seeds while the latter are contained in a tower, or by simply intermixing the solvent and seeds in a chamber of suitable design The system of extraction by means of successive batches of pure solvent is generally referred to as "multiple extraction"

The last portions of miscella recovered in the multiple extraction process will naturally be very lean in oil Hence these portions may well be substituted for fresh solvent in the initial treatments of fresh seed In this way, each portion of solvent is made to perform a double duty, and the amount of solvent to be recovered eventually from the oil is decreased ac

cordingly A batch extraction system set up in such a manner as to utilize the principle of solvent re use to the best possible advantage is designated as a "batch countercurrent system" In this system, a battery of extractors is provided, and the solvent is used to treat the contents of each extractor in succession Each time that a batch of miscella is drained from an extractor it is used to treat a batch of seeds which have previously been extracted with a richer miscella On the other hand, the drained seeds are each time extracted with a leaner miscella Thus the seeds are treated with batches of solvent of progressively decreasing oil content, until they are finally extracted with fresh solvent and discharged, while the solvent is brought into contact with batches of seed of progressively increasing oil content until it finally encounters fresh seed and is then discharged as the finished miscella In this way, the miscella is brought out of the system at a uniformly high oil content If there are a large number of extractors in the battery, the effect approximates that of mixing the solvent and oil in continuously moving countercurrent streams

Although batch countercurrent extraction may theoretically be brought to an efficiency approaching that of continuous countercurrent extraction, by sufficiently increasing the number of extractors, the system thereby becomes very involved In practice, therefore, solvent extraction is carried out on the largest scale only in continuous systems, which are entirely automatic in operation Such systems achieve the highest economy of steam, power, labor, and materials. Their adaptability is limited only by the mechanical difficulties involved in moving the seed mass and the miscella in opposite directions with free intermixing, and in effecting a final separation of the miscella and the seed particles

If it is assumed in batch extraction that a constant volume of miscella is retained by the seeds after each drainage period and this volume is known, it is easy to calculate the number of extractions required to reduce the oil content of the seeds to any given level,[36] in the case of either multiple or batch countercurrent extraction Actually, however, the retention of miscella *is not usually constant, but is variable for different solvent–oil ratios*, presumably because of the effect on drainage of such factors as viscosity and surface tension of the miscella This circumstance renders calculations highly involved but Ravenscroft[37] has introduced a graphical method for estimating the number of extractions required for a given recovery of oil which is applicable in the case of variable oil retention Ravenscroft assumes that miscella is retained only on the surface of the solid particles, and refers to this retention as "entrainment" However, his treatment is equally valid for miscella absorbed within the particles, so long as there is

[36] L F Hawley, *J Ind Eng Chem*, **9**, 866–871 (1917) L Silberstein, *Ind Eng Chem* **20**, 899–901 (1938) S D Turner, *ibid*, **21**, 190 (1929)

[37] E A Ravenscroft, *Ind Eng Chem*, **28**, 851–855 (1936)

equilibrium between the miscella within the particles and without In the case of continuous countercurrent extraction, differences in oil concentration in the miscella within and without the seed cannot be ignored, since here equilibrium conditions do not exist

The rate of the *interdiffusion process*, by which solvent–oil replaces oil in the interior of the seed particles, is important in its relation to the time required to approach equilibrium in each stage of a batch extraction process In the case of continuous extraction it is of even greater importance, as it largely determines the efficiency or capacity of the extraction equipment In the past, mathematical data relative to diffusion have been almost completely lacking, but recently a limited amount of information has become available, through the investigations of Boucher, Brier, and Osburn[19] These workers studied the batch and continuous extraction of soybean oil from thin porous clay plates, as well as soybean flakes, by means of chlorinated solvents In all cases they found the extraction rates to be determined purely by the resistance of the material to internal molecular diffusion Liquid–film resistance to diffusion at the surface of the solid particles was apparently negligible The rate of extraction, or the time required for extraction of a given fraction of the absorbed oil, could thus be related, by means of suitable equations, to the area and thickness of the plates, their absorbent capacity, and a diffusion constant characteristic of the oil and solvent at a given temperature The diffusion constant was found to be a simple function of the product of the viscosities of solvent and oil, and otherwise independent of the relative proportions of solvent and oil

According to the data of Boucher *et al*, in the case of a homogeneous material in the form of platelets of uniform thickness, a plot of log E against t (where E is the fraction of oil remaining unextracted, and t is extraction time) should yield a curve which is linear below $E = ca\ 0\ 5$ Such curves were actually obtained in the extraction of clay plates, but in the extraction of soybean flakes it was observed by Osburn and Katz[18a] and by King, Katz, and Brier[38] that curves were obtained which were continuously concave upward from the time axis This would indicate the simultaneous operation of two distinct processes of diffusion, in one of which the oil is removed much more readily than in the other In a typical series of experiments, from 10% to 30% of the oil was extracted with an apparent diffusion coefficient of 5×10^{-7} sq ft per hr, while 70% to 90% was extracted with an apparent coefficient of 4×10^{-6} sq ft per hr There was a tendency for the fraction represented by the lower coefficient to be larger as the thickness of the flakes was increased

It was suggested that the major fraction of easily extractable oil was derived from cells ruptured during the rolling operation, whereas the minor,

[38] C O King D L Katz and J C Brier, *Trans Am Inst Chem Engrs*, 40, 533 556 (1944)

difficultly extractable portion consisted of oil from unruptured or partially ruptured flakes However, the possibility was recognized of the observed effects being caused by other forms of structural heterogeneity in the rolled flakes

The theory of diffusion in oil extraction, as well as other theoretical aspects of the process, is discussed at some length by Schonfeld [39]

Since the diffusion rate is directly proportional to both the surface area of the seed particles and the oil and solvent concentration gradients from the center of the particles to their surface, the size of the particles determines to a large extent the rate at which they can be extracted In the case of seed flakes both the area and the concentration gradients are in inverse proportion to the flake thickness The extraction rate, therefore, varies inversely with the square of the flake thickness It is obvious, therefore, that the flakes should be made as thin as is consistent with otherwise good practice However, flakes which are excessively thin are likewise fragile, and inclined to break up during extraction, to form fines which retard the circulation of solvent through the seed mass, and are difficult to separate from the miscella In practice, therefore, a compromise must be made between the opposed conditions of thinness and strength The thinness to which the flakes may be rolled depends upon the design of the extraction equipment [10] In systems such as the Bollman, where the flakes are not mechanically agitated during extraction a thickness of 0 0055 to 0 008 inch is satisfactory Systems such as the Hildebrandt require a flake 0 009 to 0 015 inch thick because of the mechanical handling to which the flakes are subjected in contact with the solvent

(c) Solvents for Oil Extraction

Much the most common solvents used for oil extraction are light petroleum fractions, recovered from natural gas The composition of these so called extraction naphthas is discussed by MacGee,[40] and a detailed analysis of one widely used product has been given by Griswold, Van Berg, and Kasch [41] European extraction plants have commonly used a naphthenic base product consisting largely of cyclohexane, and boiling within the range of about 160° to 185°F The extraction naphthas produced in the United States are paraffinic in nature Different grades are available which consist principally of normal pentane, with a boiling range of 83° to 100°F , normal hexane with a boiling range of 140° to 160°F normal

[39] H Schonfeld, in *Chemie und Technologie der Fette und Fettprodukte* Vol I, *Chemie und Gewinnung der Fette* Edited by G Hefter and H Schonfeld Springer, Vienna 1936, pp 749–753

[40] A E MacGee *Oil & Soap* 14, 324–327 (1937)

[41] J Griswold C F Van Berg and J E Kasch *Ind Eng Chem* 35, 854–863 (1943)

heptane, boiling from 186° to 212°F.; and mixed octanes, boiling from 212° to 284°F. Of these, the normal hexane product is generally preferred for the solvent extraction of oil seeds, even though its boiling point is perhaps slightly lower than might be desired. The heptane product boils at rather too high a temperature to be readily removable from the meal and the oil. It would of course be possible to produce a solvent with a boiling range similar to that of the European naphtha by blending the hexane and heptane fractions, but as pointed out by MacGee,[40] such a blend would be less satisfactory than either the pure hexanes or heptanes, since it would combine the tendency of the former to be lost by volatilization with the tendency of the latter to be retained in the oil. Higher boiling fractions may be advantageously used for special purposes, as for example, the

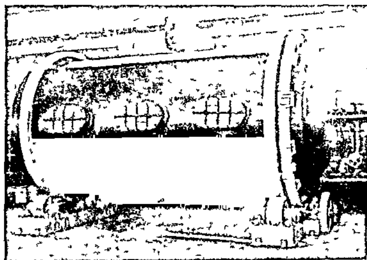


FIG 51 —Rotary extractor, for extraction of castor pomace, etc (Courtesy *The C. O Bartlett & Snow Co*)

extraction of castor oil, which is not miscible with hydrocarbons at low temperatures.

Although solvent losses in American plants employing hexanes for extraction are inclined to be higher than in European plants using a higher boiling product, they are not excessive, and in well-operated soybean extraction plants do not exceed about 2 gallons for each ton of seed processed At this rate, charges for solvent loss are inclined to be rather less than for labor, power, or steam [34]

The American-produced extraction naphthas are substantially free from nitrogen- or sulfur-containing compounds and unsaturated hydrocarbons, and leave a residue upon evaporation of less than 0.0016%. They are sufficiently stable to be re-used indefinitely, are cheap, and are available in practically unlimited quantities. The only serious disadvantage to their use is their extreme flammability. Rather elaborate precautions are

required to avoid explosion hazard in the plants in which they are used The customary safety measures followed in such plants are discussed in detail by Bonotto [42]

The use of noninflammable chlorinated solvents, such as trichloro ethylene, has often been proposed as a means of avoiding the hazard of explosion in solvent extraction plants, but so far the high cost of such solvents has prevented their being used extensively Trichloroethylene boils at 188° to 190°F

Carbon disulfide is used for the extraction of olive oil "foots" from olive press cake in Europe, but it cannot be considered a desirable solvent Acetone is used to some extent for the extraction of wet materials, such as fish livers, as is ethyl ether [37]

(d) *Batch Extraction*

Batch solvent extraction is principally used for the recovery of relatively expensive oils, such as pharmaceutical oils, from small batches of material, for the final recovery of oil from press residues, or for other purposes where the tonnage of material handled does not justify the expense of installing a continuous system The largest single use of batch extractors at the present time is probably for processing of the castor pomace remaining from the cold pressing of castor beans Batch extractors are also used extensively for extracting garbage grease, meat scraps, and fish liver oils

Batch extractors vary greatly in design An extractor which is popular in the castor oil industry (Fig 51) consists of a large horizontal drum (18 by 8 5 ft) mounted on rollers by means of which the drum can be slowly rotated on its longitudinal axis Inside the drum is a horizontal, perforated, metal strainer covered with a filter mat of burlap, which extends the length of the drum and divides it into two compartments, one of which is much smaller than the other The large compartment receives a charge of 10 to 12 tons of solid material and 4000 to 5000 gallons of solvent, which are gently mixed by rotation of the drum After mixing is completed, the solvent is allowed to drain into the smaller compartment by gravity, from which it is continuously pumped during the drainage period Five to seven successive extractions suffice to reduce the oil content of castor pomace from about 15% to 1 5%

The extractor commonly used for the extraction of garbage consists of a vertical cylindrical kettle, with a large ratio of diameter to depth, equipped with a vaportight cover, a steam jacket, and a vertical low speed agitator The most popular unit is about 4 feet, 6 inches in height, and 10 feet in diameter, and takes a charge of 3 to 5 tons of material This extractor is suitable also for the extraction of other relatively wet materials, as the material may be dried and extracted in the same vessel

[42] M Bonotto, *Oil & Soap*, **14**, 30–33 (1937)

Solvent systems are used to some extent for the extraction of fish liver oils, as well as fish oil The equipment used for this purpose is described by Brocklesby [14] A number of other types of batch extractors are described by Werth [43] The extraction of miscellaneous oil containing materials, as well as oil seeds, has been developed to a much higher degree in Europe than in the United States

(e) Continuous Solvent Extraction

Most of the large continuous solvent extraction systems in actual operation are of European, and particularly German design, although there are a few of American origin Goss[3a] in 1941 estimated the total capacities of the different systems operating in the United States and elsewhere in the world to be as indicated in Table 140 This tabulation does not include

TABLE 140

System	Origin	Oil seeds or oil seed press cakes (short tons/24 hours)	
		World capacity	U S capacity
Bollman (Hansa Muhle)	German	3 100	750
Hildebrandt	German	2 200	430
Fauth	German	800	0
Allis Chalmers (modified Bonotto)	American	170	170
French (modified Bollman)	American	130	130
Ford	American	75	75

[a] W H Goss Chem & Met Eng, 48, No 4 80–84 (1941)

installations of certain extractors then of minor importance, such as the Miag and Kennedy

The Bollman or Hansa Muhle extractor[44] (Fig 52) has the appearance of an enclosed bucket elevator It consists of a number of baskets (usually 38) with perforated bottoms, which are supported on endless chains, within a gastight housing The flaked oil seeds are conveyed by a screw into a closed charging hopper at the top of the housing, the completely filled conveyor tube serving as an effective vapor seal against the solvent vapors inside the extractor The baskets are continuously and very slowly raised

[43] A van der Werth, in *Chemie und Technologie der Fette und Fettprodukte* Vol I, *Chemie und Gewinnung der Fette* Edited by G Hefter and H Schonfeld Springer, Vienna, 1936, pp 677–748

[44] H Bollman German Pats 303 846 (1919) and 322,446 (1920), British Pat 156 905 (1921) Hansa, Mühlenbau und Industrie, A G German Pat 670 283 (1939) British Pat 507,465 (1939)

and lowered, at the rate of about one revolution per hour. As each basket starts down the descending side of the apparatus, a charge of about 800 pounds of seed is automatically dropped into it, from the charging hopper. Extraction is effected by the percolation of solvent through the seed during their passage from the top to the bottom, and again to the top of the apparatus. As the baskets containing the spent flakes ascend to the top of the housing, on the opposite side from the charging hopper, they are automati-

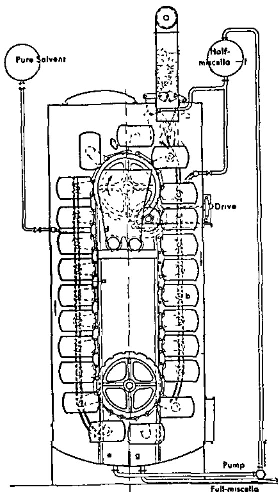


Fig 52 —Bollman extractor.

cally inverted, and the contents are dumped into a discharge hopper, from which they are conveyed by means of screw conveyors to the meal driers.

Fresh solvent at the rate of approximately one pound of solvent per pound of seed is sprayed into a basket near the top of the ascending line of baskets, from which it percolates by gravity through the lower baskets, in countercurrent flow. The miscella from this side, termed the "half-miscella," is collected in a sump in the lower part of the housing. A pump

continuously withdraws it from the sump and sprays it into the topmost basket of the descending line. From this basket it percolates downward through the lower baskets, similarly to the fresh solvent introduced on the other side of the system and is collected in a separate sump as "full miscella." The full miscella is freed from fine seed particles and solvent, to yield the finished oil, by means which will be described later.

The meal dryers used in connection with the various extraction systems, for removal and recovery of absorbed and entrained solvent from the spent flakes, do not differ materially in principle or design from one system to another. The dryers used with the Bollman extractor consist of a series of horizontal, steam jacketed tubes, through which the flakes are propelled by means of screws. The final unit of the dryer system consists of a larger drum or "deodorizer" to which steam is admitted to assist in removing the last traces of solvent. The vapors from the dryers and the steam from the deodorizer are passed through a dust separator, condensed, and then passed to the solvent–oil separator provided for recovery of solvent from the steam used in the miscella stripping column.

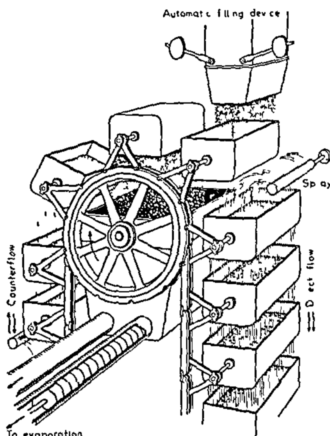


FIG. 53.—Filling device, Bollman extractor

Extractors of the Bollman type are said to have been built in sizes having

capacities of from 50 to 500 tons per day. The basket capacity mentioned above refers to that of the largest size

The American made French extractor is very similar to the Bollman extractor in all essential respects

The Hildebrandt extractor[45] (Fig 54) is built in the form of two vertical tubes, interconnected at the bottom by a third horizontal tube Each of the three tubes is provided with an independently driven screw conveyor,

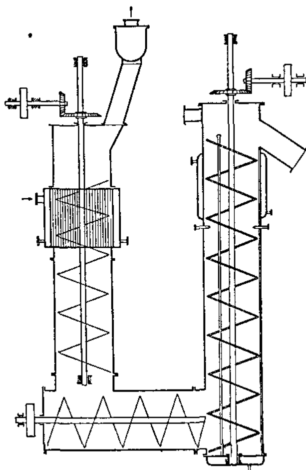


FIG 54 —Hildebrandt extractor

the flights of which are perforated, in order to retain the seed flakes, but permit the passage of solvent or miscella In operation, the system is kept flooded with solvent and miscella, to a level near the tops of the vertical tubes The seed are fed continuously to the extractor at the top of one of the two vertical legs and are slowly propelled by the screws down this leg into the solvent (miscella) across to the second leg, and up above the level

[45] K. Hildebrandt German Pats 528 287 (1931) and 547,040 (1932), U S Pat 1,961,420 (1934)

of solvent in the latter, where they are drained and then discharged The solvent is introduced near the top of the second leg, and is pumped counter current to the movement of the flakes The finished miscella discharges near the top of the first leg, through a section of the tube which is provided with fine vertical slots to restrain the passage of flake particles There is but a slight clearance between the conveyor screw and the sides of the strainer section, so that the inside of the strainer is continuously wiped clean by the action of the screw

In the Fauth system,[46] extraction is carried out continuously, but in a number of successive stages, with the miscella being squeezed from the seed mass after each stage The most recently described form[33] of the Fauth extractor employs a continuously moving conveyor belt of filter cloth, which carries the seed through a long, totally enclosed chamber A special disintegrating device similar to an ordinary food chopper effects a preliminary mixing of the seed particles and miscella, and discharges the mixture to the conveyor Solvent or miscella is sprayed upon the seeds at intervals along the conveyor, it percolates through the seed and filters by gravity into receivers placed beneath the belt At intervals between the spray nozzles the belt and its contents pass between weighted rolls, which press the solid material substantially free from miscella The lower roll is in each case perforated, so that most of the expressed miscella filters through its surface into a suitable receiving trough Revolving rakes between each set of rolls serve to break up the pressed and compacted material and mix it anew with miscella or solvent from the spray system The miscella drained and pressed from the seeds in each stage is collected in separate receivers, and the spraying devices and receivers are so connected that there is a countercurrent flow of seeds and solvent The spent material issuing from the last set of rolls is discharged into a hopper, from which it is conveyed to the meal dryers On its return, the conveyor belt is first scraped free of solid material, is then cleaned by a spray of solvent passing through it in a reverse direction to the filtered miscella, and is finally dried by being passed over a heated drum

Other models of the Fauth extractor utilize the principle of alternate lixiviation and pressing of the material to be extracted, but accomplish the former operation in a series of drums equipped with moving metal screens

The Fauth system is particularly adapted to the extraction of seeds of high oil content, which are inclined to disintegrate during treatment It is said to be successfully used in Europe for the extraction of such difficult materials as unpressed peanuts and copra

The extractor patented by Bonotto[47] consists of a tall, vertical, cylindrical

[46] P L Fauth, German Pat 356 304 (1919), Brit Pat 157 155 (1921)

[47] M Bonotto (to American Soya Products Corp) U S Pats 2 086 181 (1937) (to Extractol Process, Ltd) 2,112,805 (1938), 2 156 236 (1939), 2,184 248 (1939)

column fitted with a series of equally spaced circular discs, which are rotated by a common central shaft These plates serve to maintain the seed mass in a well dispersed condition throughout the length of the column, with the elimination of packing and bridging of material The seed to be extracted are fed to the top of the column, from where they fall by gravity through the miscella to the topmost disc or plate As the plate assembly rotates, the seed are swept from each plate by a stationary scraper arm, through a slot in the plate, to fall to the surface of the plate immediately below Thus the seed are dropped successively from one plate to another, the arrangement of slots being such that they describe a slow spiral path down the column The solvent is introduced at the bottom of the column and after flowing countercurrent to the seeds is withdrawn through a strainer near the top of the column The spent flakes reaching the bottom of the column are discharged by a screw mechanism operating against a loaded cone type orifice This mechanism compresses the flakes sufficiently to form a plug which is impervious to the liquid above it, and of course presses the flakes almost free of solvent in the same operation

The Allis Chalmers extractor[34] is a modified Bonotto type, in which the plug forming mechanism is replaced by a conveyor of the screw or Redler type, operating in an inclined side tube This conveyor takes the flakes from the bottom of the column and elevates them above the level of the solvent, where they are drained and then discharged An extractor of this type is said to operate effectively at a ratio of 0 6 pound of solvent per pound of seeds extracted

In the Kennedy system,[48] (Fig 55) extraction is carried out in a series of rounded bottom tanks placed side by side in a single vaportight housing A four bladed paddle wheel with perforated paddles revolves in each tank, with a close clearance being maintained between the paddle blades and the circular contour of the tank bottom The seed particles are introduced at one end of the series of tanks, and are transferred from one tank to another and finally discharged from the last tank by the scooping action of the various paddles The solvent and miscella are pumped from tank to tank, countercurrent to the movement of the seed

The Ford extractor[49] is similar in principle to the Hildebrandt, but employs a long inclined tube connected to a shorter vertical tube, in place of the U tube arrangement of the latter system It was designed specifically for the extraction of soybeans The flaked beans are introduced at the top of the short vertical tube, to fall to the bottom of the inclined tub The solvent level stands near the top of the vertical tube and about half way up the inclined tube The flakes are extracted as they are propelled up the inclined tube by a screw conveyor, against the countercurrent flow of the solvent

[48] A B Kennedy, U S Pat 1 628 787 (1927)
[49] H Joyce *Oil & Soap* **12**, 68 70 (1935)

In the Böhm system,[50] extraction is carried out in a series of superimposed pans inside a vaportight housing The pans are arranged in staggered positions in two adjacent vertical banks, each pan is provided with an outlet chute discharging into the pan next below it, and a baffle for directing the contents of the pan to the chute The sides of the pans are solid, and fixed in position, but the bottoms are perforated and attached to vertical rotating shafts In operation, the seeds are delivered to the topmost pan, and are transferred from pan to pan down the two columns by the rotation of the pan bottoms and the action of the fixed scraper baffle in each pan Each pan is provided with spray nozzles for directing miscella or solvent onto the surface of the seed, and a trough for receiving the miscella after it has percolated through the seed and the perforated pan bottom A series of pumps is provided on the outside of the extractor proper, to withdraw the miscella from each receiving trough and spray it into the pan next above the one from which it was removed The spent flakes from the last pan

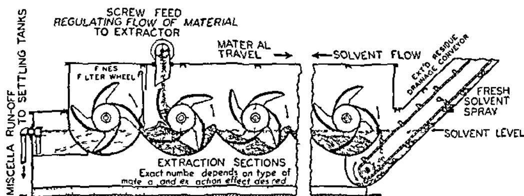


Fig 55—Kennedy extractor (Courtesy *The Read Machinery Co, Inc*)

discharge into a chute from which they are conveyed to the meal driers The miscella from the top pan is run to the usual filters and stills for separation of the solvent and the oil

The Miag extractor[51] is built in the form of a large wheel, vertically mounted, which revolves inside a closely fitting annular casing The wheel is provided with perforated cells which carry the seed countercurrent to solvent flowing in the annulus

Many other continuous solvent extraction systems have been patented, and some have been used to a limited extent A considerable number of these extractors are described by Werth [43]

(*f*) *Recovery of Solvent*

An essential part of any extraction system consists of rather elaborate equipment for the efficient recovery of solvent from the extracted meal and the miscella

[50] E Böhm, German Pat 578 704 (1933)

[51] Miag, Mühlenbau und Industrie A G, German Pat 576 209 (1933)

In practically all systems the miscella as withdrawn from the extracto contains a certain amount of fine seed particles or meal The usual prac tice is to remove the meal by filtration of the miscella, employing closed bag type filters or filter presses for the purpose In at least one American plant, however, meal particles are separated from the oil *after* the latter has been freed of solvent [34] Settling is of limited value for clarification of the miscella because of the slow settling rate of very small meal particles in an oil–solvent mixture Data on the settling rates of soybean particles 1 to 100 microns in size in hexane–soybean oil solutions of different strengths have been published by Bilbe [34]

The equipment used for recovery of solvent from the clarified miscella varies considerably in different systems In some plants the miscella con taining about 25% oil and 75% solvent is passed first through one or two evaporating chambers equipped with steam coils where the solvent content is reduced to 50% to 55% It is then concentrated to about 90% to 95% oil in a steam heated evaporator of the "falling film" type, and is finally freed from the last traces of solvent by passage through a stripping column of either the packed or tray and bubble cap type The vapors from both the first and second stages of evaporation are condensed in water-cooled condensers and returned to solvent storage The steam from the stripping column is likewise condensed, the water and the solvent are separated by gravity, and the recovered solvent re used In order to produce an oil of good quality, it is essential for the entire operation of solvent removal to be conducted rapidly and at a low temperature This is best accomplished if evaporation of the solvent is carried out in successive stages, with at least the last stage of steam stripping being conducted under reduced pressure

In other systems the filtered miscella is superheated and then passed to an evaporator of the "flash" type for removal of the bulk of the solvent, before it is put through the stripping column In any case, regardless of the methods employed for evaporating the bulk of the solvent, the last traces must be stripped out with steam, if complete removal is to be accom plished at an acceptably low temperature In well designed systems, the temperature of the oil or miscella does not exceed 200° to 212°F at any time

Some economy of heat is achieved in some installations by employing heat exchangers to transfer a portion of the heat from the vapors leaving the evaporators to the feed miscella or to the fresh solvent flowing to the extractor Where a hexane fraction is used as the solvent, the actual extraction is carried out at a temperature of about 120°F, and the solvent must of course be heated to this temperature before it enters the extractor In most installations all air vented from the system is passed through towers charged with activated charcoal before it is discharged to the atmosphere The absorption towers are installed in pairs, so that one may remain in

fruit bunches are first sterilized, upon receipt at the extraction plant, to inactivate lipolytic enzymes and loosen the fruits from the bunch sufficiently to permit threshing Sterilization is conducted in large autoclaves under an injected steam pressure of not more than 30 pounds, for about one hour Sterilization requires approximately 350 to 400 pounds of steam per (long) ton of bunches Normally, the sterilized bunches lose approximately 10% of the weight of the fruit as water If the oil is to be subsequently extracted by means of centrifuges, excessive drying of the fruit is avoided If the oil is to be expressed in hydraulic presses, however, a relatively dry fruit is desirable, and the normal sterilization period may be followed by one half hour of vacuum treatment

The sterilized bunches are run through strippers or threshers, to separate the fruit from stems and stalks, after which the separated fruit is treated in digesters Digestion is different for press and hydraulic methods of extraction If the material is to be pressed, digestion is carried out in an open, stirred, steam jacketed kettle, with further dehydration occurring during the operation If it is to be centrifuged, the digester is closed, and digestion is carried out under a few pounds steam pressure The contents of the digestor are discharged either to the presses or centrifuges, according to the system used In either case, there is no separation of pulp and kernels prior to expression of the oil

The presses used for palm fruits are of a special steam heated cage design The centrifuges used are of the basket type, and are totally enclosed and provided with a nozzles for the injection of steam during the extraction operation They are ordinarily run 2–3 minutes without steam, then about 6 minutes with steam, then 2 minutes without steam

The centrifugal and hydraulic press systems are equally efficient insofar as oil recovery is concerned, each recovers 85–90% of the oil in the pulp In the case of centrifuged extraction, a residue is produced containing about *8 5% oil, 50% moisture, and 41 5% solid material The cost of the* plant is approximately the same for the two systems, and charges for labor and power are not significantly different The press system expresses more oil, but the oil contains more solid material, and there are greater losses of oil in subsequent purification

The extracted oil is purified by being heated in tanks with open steam and then either settled or centrifuged Hydraulically pressed oil must have 40% of water added prior to purification, whereas centrifuged oil requires no such addition A 250 gallon charge of the oil–water–pulp mixture yields 160 gallons of oil, 20 gallons of sludge, and 70 gallons of water by centrifugation The oil content of the water is 0 05–0 10 pound per gallon

It is possible, by means of a secondary pressing of the pulp residue, to recover approximately 50% of the remaining oil, but such treatment is not economically feasible under all conditions of the palm oil market

CHAPTER XVI

REFINING AND BLEACHING

1. Introduction

The crude fats and oils produced by rendering, expression, or solvent extraction, contain variable amounts of nonglyceride impurities In the case of high grade animal fats and certain vegetable oils, such as coconut and palm kernel oils, these impurities consist principally of free fatty acids There are significant amounts of other substances, however, in most vegetable oils, as well as in animal fats which have been rendered from low-grade materials Thus, for example, Jamieson and Baughman[1] reported the following in crude cottonseed oil raffinose, pentosans, resins, proteoses, peptones, phospholipins (phosphatides), phytosterols, phytosteroline, inosite phosphates, xanthophyll, chlorophyll, mucilaginous substances, and free fatty acids

Not all of the impurities of crude oils are undesirable The sterols are colorless and heat stable, and for all practical purposes, inert, hence they pass unnoticed unless present in unusually large amounts Tocopherols and certain related compounds perform the important function of protecting the oil from oxidation For this reason they may be classed as highly desirable constituents of most oil and fat products However, most of the other impurities are objectionable, since they render the oil dark colored, cause it to foam or smoke, or are precipitated when the oil is heated in subsequent processing operations The object of refining and bleaching[2] is to remove the objectionable impurities in the oil with the least possible damage to either the glycerides, or the tocopherols or other antioxidants

Sterols, and certain constituents which are present in traces only, including tocopherols, hydrocarbons, chlorophyll, carotenoid pigments, and ketonic or other odoriferous substances, are relatively little affected by ordinary refining treatment, and hence are found even in well refined oils However, free fatty acids, phosphatides, carbohydrates, nitrogenous or proteinaceous compounds, and resinous and mucilaginous substances are

[1] G S Jamieson and W F Baughman, *J Oil & Fat Ind*, 3, 347–355 (1926)

[2] General references H K Dean, *Utilization of Fats* Chemical Pub Co, New York 1938 T P Hilditch, *Industrial Fats and Waxes* 2nd ed, Baillière, Tindall & Cox, London, 1941 G S Jamieson, *Vegetable Fats and Oils* 2nd ed, Reinhold, New York, 1943 G Hefter and H Schonfeld *Chemie und Technologie der Fette und Fettprodukte*, Vol II, *Verarbeitung und Anwendung der Fette* Springer, Vienna, 1937

ordinarily removed by refining The term "refining" as used here, refers to any purifying treatment exclusive of bleaching or deodorization The term "bleaching" is reserved for such treatment as is designed solely to reduce the color of the oil, whereas "deodorization" refers to processes which have as their primary object the removal of substances giving rise to odors and flavors

A method was developed by Wesson[3] and modified by Jamieson[4] whereby an estimate could be made of the total amount of fatty acids and other substances which are normally removed from an oil by alkali refining The content of these substances in the oil, often referred to as the "absolute loss," or the "Wesson loss," is of some significance in refining theory and practice, inasmuch as it represents a minimum value beyond which the refining loss of the oil cannot be reduced The Wesson loss in crude cottonseed, soybean, peanut, and corn oils is ordinarily from 1–3% greater than the free fatty acid content of the oil

2. Applications

Some oils and fats are seldom given any kind of purifying treatment Butterfat, oleo oil, and olive oil are neither refined nor bleached in the ordinary course of manufacture, although in rare instances the refining process may be applied for the reclamation of off grade or badly deteriorated materials

Most of the lard on the market is not refined in the proper sense of the term The product known to the trade as "refined lard" has merely been clarified and solidified, with the application of a light bleaching treatment, in some cases, by means of a bleaching clay or carbon A few special lard products which are hydrogenated or deodorized are also alkali refined Small amounts of tallow or oleo stock are consumed without being refined, and considerable quantities of unrefined oleostearine are used in the manufacture of blended type shortenings and margarines of the "puff paste" type Inedible animal fats used in the manufacture of soaps are in some cases refined and in other cases unrefined In the treatment of soap fats refining is chiefly valuable because of its beneficial effect on the color of the fats Soap fats are almost invariably bleached

In some parts of the world, particularly in Africa, Southern Europe, and the Orient, considerable quantities of oil seeds yielding a relatively pure oil, such as peanut, sesame, rapeseed and soybean, are cold pressed, and the resulting oil is used for edible purposes, like olive oil, without further processing treatment Oils which are to be deodorized and marketed as neutral salad or cooking oils, as well as vegetable oils which are to be converted into shortenings or margarines, are almost invariably alkali refined

[3] D Wesson, *J Oil & Fat Ind*, **3**, 297–305 (1926)

[4] G S Jamieson, *Vegetable Fats and Oils* 2nd ed, Reinhold, New York, 1943

Free fatty acids are objectionable in all of these products, because of their relative instability to heat and oxidation The higher fatty acids are so insoluble as to be practically tasteless, hence oils containing large proportions of these may be rendered at least temporarily neutral by deodorization alone The fatty acids of coconut oil and other lauric acid type oils are sufficiently soluble, however, to taste strongly, hence it is essential that these oils be rendered substantially free of free acids by alkali refining before they are used in food products

Vegetable paint oils are not usually alkali refined, since in these oils a moderate content of free acids is unobjectionable They are frequently acid or water washed however, in order to completely remove material which would precipitate under heat treatment The removal of this so called "break material" is essential in varnish oils, the higher grades of which are often refined with alkali

Whale, fish, and other marine oils, with the exception of fish liver oils, are refined before they are manufactured into edible products, since such products are invariably hydrogenated and deodorized Fish liver oils are preferably not alkali refined because of the tendency toward vitamin A adsorption of soaps formed *in situ* in the oil [5]

3 Refining by Hydration

Certain oil impurities, such as phosphatides, proteins or protein fragments, and gummy or mucilaginous substances, are soluble in the oil only in an anhydrous form, and can be precipitated and removed if they are hydrated The hydration and removal of phosphatides from soybean oil has been described previously, in connection with the solvent extraction of soybeans Other vegetable oils, and particularly corn and cottonseed oils, are also sometimes subjected to a similar "degumming" process prior to alkali refining, in order to reduce the refining loss

The water washing or degumming process is similar to continuous alkali refining, except that warm water is used in place of the alkali The water and oil are emulsified together in a continuous mixing device, and after a suitable holding time the hydrated substances and the excess water are removed by continuous centrifugation In some cases a weak solution of sodium carbonate, sodium bicarbonate, trisodium phosphate, or other weak alkali, is substituted for the water, and the use of sodium chloride solution, boric acid solution, etc has also been suggested in various patents

While the removal of phosphatides prior to alkali refining is definitely advantageous in the case of soybean oil and corn oil, there is some division of opinion as to the value of water washing as applied to crude cottonseed oil A considerable proportion of the nonoil constituents of cottonseed oil can

[5] H N Brocklesby, *The Chemistry and Technology of Marine Animal Oils* Fisheries Research Board of Canada, Ottawa, 1941, p 259

be precipitated by hydration, but there is also some removal of substances which inhibit the emulsification of neutral oil in alkali refining, so that the washed oil is relatively difficult to refine Thus the reduction in refining loss is not as great as might be supposed Also there is some loss of neutral oil in water washing While there is a considerable market for soybean phosphatides, no important use has been developed for the gummy materials which are precipitated by water from cottonseed oil There appears to be evidence that if the cottonseed is properly cooked before the oil is expressed, the advantage in water washing the oil prior to caustic soda refining is at best but slight If the oil is to be refined by the newer soda ash–caustic soda method, there is probably no benefit to be derived from preliminary water washing

As stated previously, hydrated soybean phosphatides are used in the preparation of commercial lecithin Both the manufacture and some of the uses of this product are at present rather closely controlled by patents [6] Corn oil phosphatides can be used for most of the purposes for which soybean phosphatides are suitable, but cottonseed phosphatides or gums, which are high in nonphosphatidic substances, have no especial value and are usually mixed with the cottonseed meal, and disposed of as an animal feed

The hydration method of refining is not generally used on animal fats, since these fats are for the most part substantially free of phosphatides or other hydratable substances It has some application, however, in the treatment of dry rendered fats for the removal of dissolved or dispersed proteinaceous substances, as mentioned previously in connection with the production of dry rendered lard

4. Refining by Means of Alkalies

By far the most important and generally practiced method of refining is by means of an alkali Alkali refining effects an almost complete removal of free fatty acids, which are converted into oil insoluble soaps Other acidic substances likewise combine with the alkali, and there is probably some removal of impurities from the oil by adsorption on the soap formed in the operation Also all substances are removed which become insoluble upon hydration

The alkali most commonly employed for refining oils is caustic soda, which is much more effective in its decolorizing action than weaker alkalies Caustic soda has the disadvantage, however, of saponifying a small proportion of neutral oil, in addition to the free fatty acids There is some use, therefore, of other alkalies, such as soda ash or sodium bicarbonate

[6] H Bollman, Ger Pats 382,912 (1923) and 485,676 (1929), U S Pats 1 464 557 (1923), 1,667,767 (1928), 1,776,720 (1930), 1,893,393 (1933) H R Kraybill (to Purdue Research Foundation), U S Pat 2,069,187 (1937) B Rewald, U S Pat 1,895,424 (1933).

Organic bases, such as the ethanolamines, have also been proposed as refining agents, because of their selective action toward the free acids in the oil

The technology of alkali refining is concerned with the proper choice of alkalies, amounts of alkalies and refining techniques, to produce the desired purification without excessive saponification of neutral oil, and with methods for the efficient separation of refined oil and soapstock

(a) *Influence of Surface Active Agents in the Oil*

The efficiency of alkali refining is in general judged by the refining loss and the color of the refined oil Increasing the amount of alkali improves the color of the oil, but at the same time increases the refining loss Since loss of oil in refining is in considerable part occasioned by the emulsification or occlusion of neutral oil within the soapstock, it may be markedly influenced by naturally occurring surface active substances in the oil Thus, for example, cottonseed oil with a free fatty acid content of 0 6% may have a refining loss varying from about 2 5% to 7 0%, according to its content of surface active materials

According to their specific nature, surface active materials in crude oils may either promote or inhibit the occlusion of neutral oil [7] The presence of phosphatides, proteins, etc , is in general inclined to make the refining loss high On the other hand, Royce and Lindsey[8] have shown that gossypol very definitely contributes to the production of a firm soapstock and a low refining loss in cottonseed oil Some oils appear to contain a sufficient amount of diglycerides to promote emulsification and cause consequently high refining losses

(b) *Batch Refining by the Dry Method*

The dry method of refining is the one generally practiced in the United States where any kind of fat or oil is to be refined by means of caustic soda This method is termed "dry" because the oil is treated with a relatively strong lye, and the soapstock or "foots" are recovered in a solid or semisolid form, from the cooled oil It is distinguished from the "wet" method of refining, in which the soapstock is washed to the bottom of the refining kettle with considerable quantities of water, and recovered in the form of a fluid solution Dry refining has the advantage of being rapid and convenient, and of producing a concentrated soapstock It is particularly adapted to the refining of cottonseed oil, which in most cases produces a firm soapstock, free from any considerable amount of occluded oil It is less suitable for the treatment of oils such as solvent extracted soybean oil, which produce soft, sloppy foots

[7] J J Ganucheau and E L D'Aquin *Oil & Soap*, **10**, 49–50 (1933)
[8] H D Royce and F A Lindsey, *Ind Eng Chem* , **25**, 1047–1050 (1933)

The equipment required for batch refining is simple, consisting of an open tank or kettle, equipped with a two speed agitator, a steam jacket or coils for heating, and a conical bottom It is common for refining kettles to hold a full tank car of oil, or 60,000 pounds The first stage of refining is carried out at ordinary atmospheric temperature, or at a temperature sufficiently high to maintain the oil in a completely molten condition For the refining of cottonseed oil a temperature of about 20° to 24°C or 68° to 75°F is preferred, although somewhat higher temperatures have no great effect on the refining loss If the oil contains occluded air after it is pumped to the refining kettle, it must be settled long enough for the air to rise to the surface and escape, as otherwise the foots will entrain sufficient air to partially float, and thus will not settle properly to the bottom of the kettle

After the charge of oil is at the proper temperature, and free from air, the agitator is started at high speed, and the proper amount of lye is rapidly run in Agitation is then continued until the alkali and oil are thoroughly emulsified With some oils the best results are obtained if the mixing period is relatively short, *e g*, 10 to 15 minutes Other oils, of the "slow breaking" type, may be mixed as long as 30 to 45 minutes At the end of the mixing period the agitator is reduced to a low speed, sufficient only to keep the contents of the kettle stirred, and heat is applied to bring the temperature of the charge up to about 60°C, or 140°F as rapidly as possible Under the influence of the heat, the emulsion breaks, and the soap stock separates from the clear oil in the form of small flocculent particles which tend to coalesce as stirring is continued After the desired degree of "break" is obtained, agitation is stopped, heat is turned off the kettle, and the soapstock, or foots, is allowed to settle to the bottom of the kettle by gravity Settling is usually allowed to continue overnight, and toward the end of the settling period the bottom of the kettle is often cooled, by circulating water through a cooling jacket, in order to more thoroughly solidify the soapstock

When the contents of the kettle are well settled, the refined oil is drawn off the top, by means of a swinging suction pipe, leaving the foots in the form of a more or less firm mass at the bottom Removal of the last portions of oil from the top of the foots, by judicious use of the suction pipe, and by manipulating the foots with a paddle or pole, requires considerable skill on the part of the operator The refined oil contains small amounts of suspended water and soap, which must be removed before the oil is stored, in order to prevent deterioration of the stored oil through hydrolysis A common practice is to filter the refined oil through spent bleaching earth The use of spent earth, already saturated with oil, avoids loss of oil through retention on the earth If the oil is bleached before it is stored, it is of course dehydrated and freed of soap in the bleaching operation

The above procedure is not essentially altered if the fat to be refined is

tallow or other animal fat, although the entire operation must, of course be carried out at a temperature above the solidifying point of the fat

If the alkali used for refining is soda ash, sodium bicarbonate, or other alkali weaker than sodium hydroxide, refining may be carried out at a higher temperature, since there will be less danger of saponifying neutral fat The use of weak alkalies alone is of limited value in the treatment of vegetable oils, because of the failure of these to effect much decolorization of the oil They may be advantageously used for the removal of small amounts of free fatty acids from animal fats, however, particularly if the refiner wishes to avoid a lengthy separation of foots and fat by settling Thus, for example, Parsons[9] refines lard by treating the fat with a solution of sodium bicarbonate equivalent to two to three times its content of free fatty acids, dehydrating the resulting soapstock and removing the dehydrated soapstock by filtration, with the aid of diatomaceous earth Refining of oils with alkaline carbonates at lower temperatures, without dehydration of the soapstock is difficult, since severe foaming is apt to occur, the emulsions formed do not break easily and the entrainment of carbon dioxide in the foots hinders their settling

Refining by means of caustic soda will not render an oil completely neutral, but will reduce its free fatty acid content to a negligible value, *i e*, to 0 01–0 03% Oils refined with soda ash or sodium bicarbonate will usually have an acidity ranging from 0 05–0 10%

Much care must be exercised in the refining of oils containing excessive proportions of free fatty acids, *i e* above 15 20% Unskillful treatment of such an oil may result in the saponification of so large a proportion of the charge that it will be impossible to effect a separation of the foots and the oil In some cases it may be advisable to refine high acid oils in two stages, with only partial neutralization being accomplished in the first stage

In the refining of oils which yield soft foots by the dry method some refiners add a minor proportion of strong sodium silicate solution to the lye, in order to produce a firmer, harder settling soapstock

(c) *Selection of Lyes for Refining*

The selection of the proper amount and strength of lye for refining is highly important in the case of any oil or fat which is to be refined with caustic soda It might be supposed that the lye to be used could be quite simply determined upon the basis of the free fatty acid content of the oil, but such is by no means the case While a relatively pure fat like lard can be expected to exhibit a more or less predictable behavior in refining, according to its free acid content, the presence of pigments and surface active substances in most vegetable oils makes their reaction to alkali treatment extremely variable In addition to differences in the oil produced by differ

[9] L B Parsons (to Cudahy Packing Co), U S Pat 1,767,999 (1930)

ent mills, due to variations in methods of processing the oil seeds, there are also well defined variations in the characteristics of oils according to their geographical origin, and other variations according to climatic conditions, which occur from season to season Variability in the reaction of the oil to refining and bleaching is particularly marked in the case of cottonseed oil

In the choice of both lyes and refining methods, the refiner is invariably guided by preliminary refining tests conducted in the laboratory The official refining test methods of the National Cottonseed Products Association[10] and the American Oil Chemists' Society[11] serve not only to evaluate shipments of crude cottonseed oil and other oils, on the basis of their worth to the refiner, but also provide a close indication of the results to be expected from comparable treatment of the oil in the plant Thus, by refining samples of an oil with different amounts and strengths of lye, and with different times of stirring, etc , and noting the refining loss and color

TABLE 141
SODIUM HYDROXIDE CONTENT OF LYES OF DIFFERENT DEGREES BAUMÉ[a]

Degrees Baumé at 15°C	Sodium hydroxide content %
10	6 57
12	8 00
14	9 50
16	11 06
18	12 68
20	14 36
22	16 09
24	17 87
26	19 70
28	21 58
30	23 50

[a] American Oil Chemists' Society, *Official and Tentative Methods* Revised to Jan 1 1941 New Orleans 1941

of the oil obtained in each case, it is possible to determine the optimum conditions for refining the oil in the plant

It is customary to measure the strength of lye solutions for refining in terms of their specific gravity expressed in degrees Baumé The refiner ordinarily employs one of a series of lyes ranging from about 10° to 30° Bé , in 2° steps, with oils of good quality usually being refined with 12°, 14°, or 16° lye Weaker lyes are usually employed only for re refining The actual sodium hydroxide content of lyes of different strengths is shown in Table 141

Ordinarily, the refiner uses lye containing a sufficient amount of sodium

[10] National Cottonseed Products Association *Rules Governing Transactions between Members*, 1943–1944

[11] American Oil Chemists Society, *Official and Tentative Methods* Revised to Jan 1 1941 New Orleans 1941 A E Bailey R O Feuge, and W G Bickford *Oil & Soap*, **19**, 97–102 (1942)

ıydroxide to produce the color desired in the oil, and uses the strength of ye which will produce the lowest refining loss with the desired color In general, the best results are obtained with relatively weak lyes on low free atty acid oils, and with stronger lyes on high acid oils, but the exact lye o be used in any case can be determined only by trial Refiners cus omarily calculate the amount of lye required to neutralize the free fatty ıcids in the oil, and to this amount add an excess depending upon the char ıcteristics of the oil The excess is expressed in terms of dry sodium

TABLE 142

TABLE FOR THE CALCULATION OF LYES FOR REFINING

A Percentages of lyes of different strengths required to neutralize the free fatty acids in oils of varying acidity (free fatty acids calculated as oleic)

Free fatty acids %	Per cent lye of Baumé strength				
	12°	14°	16°	18°	20°
0 6	1 07	0 90	0 77	0 67	0 59
0 7	1 24	1 05	0 90	0 78	0 69
0 8	1 42	1 20	1 03	0 89	0 79
0 9	1 60	1 35	0 16	1 00	0 89
1 0	1 78	1 50	1 29	1 11	0 99
1 1	1 95	1 65	1 41	1 23	1 09
1 2	2 13	1 80	1 54	1 34	1 19
1 3	2 31	1 95	1 67	1 45	1 29
1 4	2 48	2 10	1 80	1 56	1 39
1 5	2 66	2 25	1 93	1 67	1 49
1 6	2 84	2 40	2 06	1 79	1 58
1 7	3 02	2 54	2 18	1 90	1 68
1 8	3 20	2 69	2 31	2 01	1 78
1 9	3 37	2 84	2 44	2 12	1 88
2 0	3 55	2 99	2 57	2 23	1 98
2 1	3 73	3 14	2 70	2 35	2 08
2 2	3 91	3 29	2 83	2 46	2 18
2 3	4 08	3 44	2 96	2 57	2 28
2 4	4 26	3 59	3 08	2 68	2 37
2 5	4 44	3 74	3 21	2 80	2 47
2 6	4 61	3 89	3 34	2 91	2 57
2 7	4 80	4 04	3 47	3 02	2 67
2 8	4 97	4 19	3 60	3 13	2 77
2 9	5 15	4 34	3 72	3 24	2 87
3 0	5 32	4 49	3 85	3 36	2 97
3 2	5 68	4 78	4 10	3 58	3 16
3 4	6 04	5 18	4 35	3 80	3 36
3 6	6 39	5 48	4 61	4 03	3 56
3 8	6 75	5 78	4 87	4 25	3 76
4 0	7 10	6 08	5 12	4 47	3 95
4 2	7 45	6 38	5 38	4 70	4 15
4 4	7 80	6 68	5 64	4 92	4 35
4 6	8 16	6 98	5 89	5 15	4 55
4 8	8 52	7 28	6 15	5 37	4 74
5 0	8 88	7 47	6 42	5 60	4 94

Continued

TABLE 142—*Concluded*

B Percentages of lyes of different strengths required to provide different excesses of lye (excess calculated as dry sodium hydroxide)

Excess %	Per cent lye of Baumé strength				
	12°	14°	16°	18°	20°
0 05	0 62	0 53	0 45	0 39	0 35
0 10	1 25	1 05	0 90	0 79	0 70
0 15	1 87	1 58	1 35	1 18	1 05
0 16	2 00	1 69	1 44	1 26	1 12
0 17	2 12	1 79	1 53	1 34	1 19
0 18	2 25	1 90	1 62	1 42	1 26
0 19	2 28	2 00	1 71	1 50	1 33
0 20	2 50	2 10	1 81	1 58	1 39
0 21	2 63	2 21	1 90	1 66	1 46
0 22	2 75	2 31	1 99	1 74	1 53
0 23	2 88	2 42	2 08	1 81	1 60
0 24	3 00	2 52	2 17	1 89	1 67
0 25	3 13	2 63	2 26	1 97	1 74
0 26	3 25	2 73	2 35	2 05	1 81
0 27	3 38	2 84	2 44	2 13	1 88
0 28	3 50	2 94	2 53	2 21	1 95
0 29	3 63	3 05	2 62	2 29	2 02
0 30	3 75	3 15	2 71	2 37	2 09
0 31	3 88	3 26	2 80	2 44	2 16
0 32	4 00	3 36	2 89	2 52	2 23
0 33	4 13	3 47	2 98	2 60	2 30
0 34	4 25	3 57	3 07	2 68	2 37
0 35	4 37	3 68	3 16	2 76	2 44
0 36	4 50	3 78	3 25	2 84	2 51
0 37	4 62	3 89	3 34	2 92	2 58
0 38	4 75	3 99	3 43	3 00	2 65
0 39	4 88	4 10	3 58	3 07	2 72
0 40	5 00	4 21	3 61	3 15	2 79
0 41	5 13	4 31	3 70	3 23	2 86
0 42	5 25	4 42	3 80	3 31	2 93
0 43	5 38	4 52	3 89	3 39	3 00
0 44	5 50	4 63	3 98	3 47	3 06
0 45	5 63	4 73	4 07	3 55	3 13
0 46	5 75	4 84	4 16	3 63	3 20
0 47	5 88	4 85	4 25	3 70	3 27
0 48	6 00	4 95	4 34	3 78	3 34
0 49	6 13	5 16	4 43	3 86	3 41
0 50	6 25	5 26	4 52	3 94	3 48

hydroxide, on a percentage basis, calculated on the weight of the oil Table 142 gives the percentages of lyes of various strengths which are required to neutralize different percentages of free acids in the oil, and also the additional amounts of lye required to provide sodium hydroxide in different degrees of excess The use of the table may be made clear by an example Thus it may be desired to know the percentage of 16° lye required to refine

an oil containing 2.0% free fatty acids, with 0.45% excess sodium hydroxide. Referring to the table it will be seen that the neutralization of 2.0% free acids, calculated as oleic, requires 2.57% of 16° lye. An excess of 0.45% corresponds to 4.07% of the same lye. The total amount of lye required is the sum of the two, or 6.64%.

Animal fats of good quality, and vegetable oils low in nonoil substances may usually be refined satisfactorily with 0.10–0.25% excess sodium hydroxide. Cottonseed oil is not ordinarily refined with less than 0.25% excess sodium hydroxide, and often may require as much as 0.60% excess, or more, as may other vegetable oils containing a large proportion of non-glyceride substances, or animal or marine oils of poor quality.

(d) *Batch Refining by the Wet Method*

In European refineries, where most of the oils refined produce soft soap stocks, the "wet" refining method is commonly practiced. There are a number of variations of this method, but in general it involves heating the oil charge to a relatively high temperature, e.g., 150°F., mixing in the lye, and washing down the precipitated soapstock with a spray of hot water directed onto the surface of the oil. In some cases, dry salt is added with the water, to assist in breaking the emulsion of soapstock and oil, and to aid in settling the soapstock. Several successive water washes are required to complete the substantial removal of soap from the oil. After each wash, the oil must, of course, be thoroughly settled.

The wet refining method is little used in the United States, except for the refining of coconut oil or other oils of the lauric acid type. The kettles used for wet refining are similar to those used for dry refining.

(e) *Continuous Centrifugal Refining*

The batch method of refining cottonseed, soybean, and other vegetable oils has been largely superseded in the United States by continuous methods, in which the separation of oil and foots is carried out in centrifuges. The continuous method has the double advantage of greatly reducing the time of contact between oil and alkali, and effecting a very efficient separation of foots and oil. Consequently it reduces to a minimum the loss of neutral oil through saponification or occlusion in the soapstock, and at the same time produces a refined oil of equally as good grade as batch methods.

The first continuous plants installed in the United States for refining cottonseed oil were sold under a guarantee that they would effect a 30% saving in refining loss over kettle refining. Results of a typical comparison between batch and continuous refining are outlined in Table 143. Each of the ten tests reported in this table was conducted upon a batch of two or three tank cars (120,000 to 180,000 pounds) of crude cottonseed oil. The batch was in each case thoroughly mixed, and then split into

equal portions, one of which was refined by the kettle and the other by the centrifugal method

Although centrifugal refining was proposed as early as 1923, by Hapgood and Mayno[12] successful continuous systems were not developed until about 10 years later, as a result of the work of James[13] and of Clayton and Thurman and associates[14] The first system installed in the United States has been described by James[15] The following is a brief description of the essential features of the method and equipment

Continuous streams of oil and lye are fed to opposite cylinders of a duplex proportioning pump, the lye cylinder of which is adjustable in volume for different percentages of lye, and provided with an indicator to show its adjustment at any time The oil and lye are discharged to a series of two or three mixers consisting of small horizontal chambers equipped with fast-revolving paddle blades Within the mixers the oil and lye are thoroughly emulsified The emulsion is then passed through an oil–hot water heat exchanger, where it is broken by being quickly heated to about 140°F Separation of the soapstock and oil is then carried out in high speed centri

TABLE 143

COMPARISON OF BATCH AND CONTINUOUS CENTRIFUGAL REFINING

Test No	FFA of oil %	Lye used		Oil refined lbs		Refining loss %		Color of refined oil units Lovibond red		Bleach color units Lov red		FFA of refined oil %		Saving of oil by cont method %
		%	°Bé	Batch	Cont	Batch	Cont	Batch	Cont	Batch	Cont	Batch	Cont	
1	1 4	4 5	16	89 550	86 880	5 3	4 0	7 9	6 7	2 4	1 7	0 010	0 035	36 5
2	1 4	4 0	16	61 250	58 150	6 6	4 4	8 2	7 2	2 2	2 0	0 015	0 030	33 3
3	2 4	6 5	16	59 950	60 350	10 0	6 6	10 8	9 4	4 5	3 4	0 010	0 030	34 0
4	1 3	4 5	16	91 100	90 550	7 0	4 9	7 3	7 3	2 0	2 0	0 010	0 025	30 0
5	2 0	6 0	16	62 350	61 350	9 2	6 1	9 5	10 0	3 0	3 2	0 015	0 045	33 6
6	1 2	4 5	16	90 150	89 650	6 8	4 35	6 4	6 6	1 9	2 1	0 010	0 030	36 0
7	2 0	7 7	16	59 900	60 650	10 0	7 8	9 5	9 5	4 0	4 0	0 010	0 020	22 0
8	1 4	4 5	16	60 000	60 400	7 6	5 1	7 2	6 6	2 1	1 9	0 010	0 010	32 9
9	1 3	4 5	16	61 050	60 550	7 4	5 1	6 3	6 3	1 6	1 6	0 030	0 020	31 0
10	2 0	6 5	16	61,300	61 650	8 5	6 3	8 3	7 6	3 0	2 5	0 030	0 040	25 8
On basis of total oil refined				696 600	693 850	7 82	5 36	8 02	7 60	2 77	2 55	0 015	0 030	31 7

[12] C H Hapgood and G F Mayno (to DeLaval Separator Company), U S Pat 1,457,072 (1923)

[13] E M James (to Sharples Specialty Co), Brit Pat 407,995 (1934), Fr Pat 743,449 (1933), Can Pat 355 720 (1936), U S Pat 2,050 844 (1936)

[14] B Clayton (to Refining, Inc), U S Pats 2,100,276 and 2,100,277 (1937), and succeeding patents B Clayton, W B Kerrick, and H M Stadt (to Refining, Inc), U S Pats 2 100,274, 2,100 275 (1937), 2,137,214 (1938) B H Thurman (to Refining, Inc), U S Pat 2 150 733 (1939) and succeeding patents

[15] E M James, *Oil & Soap*, **11**, 137–138 (1934)

fuges of the hollow bowl type which are equipped with a special distributor and vanes to introduce the mixture smoothly into the bowl without re emulsification The rate of flow of oil and soapstock to the centrifuges is constant but by the use of ring dams of suitable size a discharge is obtained which consists of soapstock on one side and oil containing a small amount of dissolved and suspended soap and water on the other Altogether not more than above three minutes elapse between the time the oil enters the proportioning pump and the time when it discharges from the centrifuges

The refined oil from the first or primary battery of centrifuges is col lected in a tank and from the tank is pumped continuously to a second tank

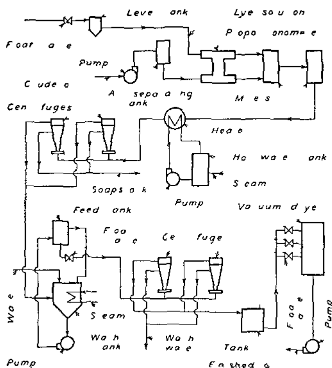


FIG 56—Flow diagram Sharples continuous refining system

equipped with a stirrer, where it is heated and mixed with about 10% of its own weight of hot water The oil water mixture at a temperature of 150–180°F is passed through a secondary battery of centrifuges, the washed oil runs into a receiving tank and the weak soap solution discharged from the centrifuges is run to the sewer In many plants in order to effect a very efficient removal of soap the washing operation is repeated at the same or a slightly higher temperature and the wash water and oil are separated in a second battery of secondary centrifuges

A standard installation employs eight primary centrifuges and four second ary centrifuges for each washing operation Such a plant has a rated ca pacity of 60,000 pounds of oil per 8 hours Actually the refining is com

pleted in about 7 hours, and an hour is allowed for shutting down the plant and cleaning the bowls of the centrifuges A layer of highly adherent foots is inclined to form on the inside of the bowls, and this must be periodically removed The centrifuges used for washing the oil, like the primary centrifuges, are of the high speed, hollow bowl type, although it is also possible to use low speed disc bowl machines for this operation Centrifuges of the latter type are unsuitable for the primary separation of oil and foots because of the thick, gummy nature of the foots

The washed oil contains traces of soap and about 0 3–0 4% of water It is dried by being fed, from a feed tank, into a continuous vacuum dryer The dryer contains a series of spray nozzles which discharge the oil into an evacuated chamber equipped with baffles Moisture is largely flashed from the oil as it enters the chamber, and the drying operation is completed as the oil runs over the baffles on its way into a hydraulic leg, from which it is pumped to storage The dried oil contains less moisture than is soluble in oil at ordinary atmospheric temperature, i e, less than about 0 12%. Ordinarily the oil is sufficiently hot by the time it reaches the dryer to require no additional heating A reduced pressure of about 1 to 2 inches is maintained on the dryer by means of steam ejectors The flow of oil to each of the spray nozzles is individually controlled by a solenoid valve The operation of the valves is coordinated with the oil feed to maintain a substantially constant pressure on the nozzles, regardless of variations in the rate of oil supply

The Clayton continuous system is essentially similar to that described above but is arranged to provide somewhat more flexibility in operation, so that it is possible to give the oil successive treatments with different lyes and to dehydrate or partially dehydrate the soapstock, etc It employs equipment items of somewhat different types, including jet type mixers and proportioners and different centrifuges and heating and drying devices

(f) *Refining with Alkalies Other Than Caustic Soda*

The use of soda ash sodium bicarbonate, and other weak alkalies for refining has been discussed above, in connection with the batch refining process The advantages and disadvantages in the use of weak alkalies may be summed up in the statement that these agents effectively de acidify the oil with less loss of neutral oil than is produced by caustic soda refining but are relatively ineffective in reducing the color of the oil In European refineries, where much of the oil refined is of varieties which are naturally light colored in the crude state, and where there is some demand for relatively dark colored edible products, the use of such alkalies as soda ash and lime for refining vegetable oils is not uncommon In the United States, however, where the chief edible oil has for many years been dark colored cottonseed oil, and where there is a vogue for very light colored oil and fat products, such alkalies are very seldom employed alone

Recently a combination soda ash–caustic soda method of refining[16] has been introduced in the United States and successfully used for the refining of cottonseed oil and other vegetable oils in at least one large refinery It effects a substantial saving in refining loss over the continuous method in which caustic soda is used alone and it would appear that it may eventually replace the latter method This process as described by Mattikow [17] is carried out as follows

The crude oil is heated by passage through a heat exchanger and is then continuously mixed with 15° to 20° Bé soda ash solution equivalent in amount to from two to two and one half times that required to react with the free fatty acids The mixture after a suitable contact period during which it may be further heated is passed to a stirred dehydrating chamber operating under reduced pressure of 0 5 to 3 0 inches where the soapstock



FIG 57 —Vegetable oil refinery employing the continuous centrifugal system (Courtesy *The Sharples Corporation*)

is dried and freed from the carbon dioxide liberated by the neutralization Following the step of dehydration the soapstock is then rehydrated by the addition of a further quantity of the same soda ash solution used for neutralization The hydrated foots are centrifugally separated from the oil, as in ordinary caustic soda refining

No emulsion is produced by the second addition of soda ash solution which serves merely to thin the foots sufficiently to permit them to flow from the centrifuges The addition of hydrating solution is regulated according to the consistency of the foots and only enough is used to cause them to discharge freely

[16] B Clayton (to Refining Inc) U S Pats 2 190 593 and 2 190 594 (1940) and succeeding patents

[17] M Mattikow, *Oil & Soap* **19** 83–87 (1942)

Soda ash treatment according to the above procedure reduces the free fatty acid content of the oil to about 0.1%, and effectively frees the oil of

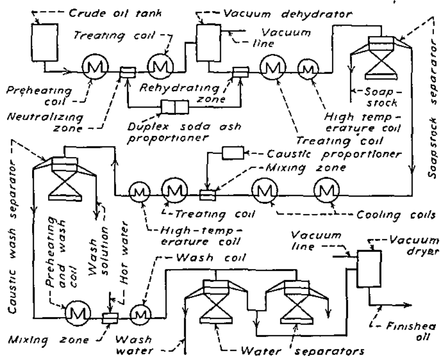


Fig. 58.—Flow diagram, *Refining, Uninc.*, soda ash-caustic soda continuous refining system



Fig. 59.—Vegetable oil refinery employing the Clayton soda ash-caustic soda continuous refining system (Courtesy *Refining, Uninc.*)

phosphatides, gums, resins, and mucilaginous and nitrogenous materials It leaves the oil relatively dark colored, however. Cottonseed oil, for example, may have a color of about 35 yellow and 18 red, on the Lovibond

scale, after reaction with soda ash The oil is given a further treatment, therefore, with caustic soda, to reduce the free fatty acids and the color to the values ordinarily obtained by refining with lye in the conventional manner In the second treatment, the oil is cooled to 70–90°F and mixed with 1–2% of 10° or 12° Bé lye The emulsion thus produced is broken by being heated to about 140°F in a heat exchanger, after which the soapstock and oil are centrifugally separated, and the oil is washed and dried in the usual way The soapstock from the lye treatment discharges as a dark, watery liquid, and may be separated in a centrifuge of the disc bowl type Due to the small volume of soapstock removed in the second operation, and the readiness with which it separates, a single centrifuge will handle the oil from several primary centrifuges

The continuous soda ash–caustic soda process will with most oils give a refining loss only about 0 6% higher than the Wesson loss Thus, for example, a cottonseed oil which refines by the kettle method with a loss of

TABLE 144
PERFORMANCE OF THE CLAYTON SODA ASH REFINING PROCESS[a]

Crude oil	FFA %	Wesson Loss %	Plant loss soda ash process %	Official cup loss[b] %
Cottonseed, Mississippi valley	0 6	2 33	2 72	4 25
Cottonseed, Southeastern	1 1	3 17	3 58	6 45
Cottonseed, Southeastern	1 8	3 80	4 41	7 35
Corn oil, dry milled	1 24	2 34	2 5	4 9
Peanut oil	0 7	1 80	2 17	4 75

[a] M Mattikow, *Oil & Soap*, 19, 83–87 (1942)
[b] Official A O C S laboratory refining test method

8 0% and by the continuous caustic soda method with a loss of 6 0%, may by this process have a refining loss of but 4 5%, thus showing a saving of oil of 25% over continuous caustic soda refining Results of test refinings of various oils, as reported by the developers of the process, are shown in Table 144

The process is said to be equally applicable to degummed and undegummed crude oils, and to produce a substantial saving of oil even in degummed crude oils with a low free fatty acid content, which give a very low refining loss by other methods

A series of recent continuous refining patents of considerable interest is that of Fash[18] In the Fash process, a special centrifugal apparatus is used to convert both oil and alkali solution to the form of mists before they are mixed for reaction It is claimed that this method enables the

[18] R H Fash (to Anderson, Clayton & Co), U S Pats 2,341 536 and 2,342,042 (1944)

refiner to obtain low refining losses and good color with the use of a very small excess of alkali

Organic alkalies have been proposed from time to time for the refining of crude oils and patents covering the use of monoethanolamine have been granted to Ashworth[19] and Hund and Rosenstein[20] However, this agent apparently has not come into commercial use

(g) Re refining of Fats and Oils

The dark colored crude oils obtained from damaged vegetable oil seeds can be reduced to a reasonably light color more satisfactorily by means of a double refining than by employing an excessive amount of lye in a single refining Off grade cottonseed oils are usually refined first with a strong lye containing from about 0 60–0 80% excess sodium hydroxide, and later before bleaching, are re refined with a smaller percentage of weak lye For some reason as yet unknown, a better reduction in color is obtained in many cases if the oil is stored for some time before re refining, than if it is re refined immediately The following plant and laboratory experiments illustrate the beneficial effect of re refining on the color of crude cottonseed oil, and also the improvement in color resulting from storing the oil after it is first refined In these experiments, all plant refinings were carried out in continuous centrifugal equipment, and all laboratory refinings were conducted by the official A O C S method Laboratory bleach tests were conducted by the official A O C S method, except that 4% of a commercial acid activated bleaching earth was used, instead of 6% of the official earth Color readings are by the A O C S method, on the Lovibond scale

The oil used in the tests consisted of a sample of crude cottonseed oil containing 5 0% free fatty acids Refined in the laboratory, this oil yielded the following results

Lye used, 13 6% of 16° Bé
Refining loss, 12 3%
Color of refined oil 35 yellow, 10 9 red
Bleach color, 35 yellow, 3 9 red

In the plant the oil was refined with results as follows

Lye used, 12 5% of 16° Bé
Color of refined oil, 35 yellow, 13 5 red
Bleach color, 35 yellow, 5 1 red

Immediately after refining, samples of both the laboratory and plant refined oils were re refined in the laboratory with 6 0% of 5° Bé lye, with the following results

[19] D I Ashworth (to DeLaval Separator Co), U S Pat 2 157,882 (1939)
[20] W J Hund and L Rosenstein (to Shell Development Co), U S Pat 2 164 012 (1939)

Color of laboratory refined oil, 35 yellow, 10 9 red
Color of laboratory refined oil, re refined, 35 yellow, 9 3 red
Bleach color of above, 20 yellow, 2 7 red
Color of plant refined oil, 35 yellow, 13 5 red
Color of plant refined oil, re refined, 35 yellow, 9 8 red
Bleach color of above, 20 yellow, 3 1 red

The following samples were stored for 30 days at atmospheric temperatures during the months of May and June

A The laboratory refined oil, filtered through paper to remove moisture
B The plant refined oil, filtered as above
C The plant refined oil, not filtered
D The crude oil

At the end of the 30 day storage period, the free fatty acid content of the crude oil (Sample *D*) had increased to 5 3% It was then refined in the laboratory with the following results

Lye used, 13 6% of 16° Bé
Refining loss, 12 2%
Color of refined oil 35 yellow 12 1 red
Bleach color, 35 yellow, 3 9 red

At the end of the 30 day period, samples *A*, *B*, and *C* were re refined with 6 0% of 16° Bé , lye, results of the re refining being as follows

Sample *A*, color of re refined oil, 35 yellow, 7 7 red
Bleach color of above, 20 yellow, 1 7 red
Sample *B*, color of re refined oil, 35 yellow, 9 3 red
Bleach color of above 20 yellow, 2 1 red
Sample *C*, color of re refined oil, 35 yellow, 9 3 red
Bleach color of above, 20 yellow, 2 1 red

It will be observed that storing the refined oil for 30 days resulted in improving the re refined bleach color of the laboratory refined oil from 2 7 red to 1 7 red, and the color of the plant refined oil from 3 1 red to 2 1 red

Some manufacturers of shortenings and other hydrogenated products make a practice of re refining their oil after it is hydrogenated The color of the product is thereby improved, and traces of colloidal nickel or nickel soaps are adsorbed by the soapstock and removed

(*h*) *Treatment and Disposal of Soapstock*

The disposition of the foots or soapstock resulting from alkali refining depends to a considerable extent upon the method of refining employed In any case, the valuable constituent of the foots consists of fatty acids which are in the form of both soaps and unsaponified oil Kettle refining by the dry method produces a soapstock which is relatively rich in fatty acids, containing usually more than 40% and often as high as 50% of total fatty

refiner to obtain low refining losses and good color with the use of a very small excess of alkali

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(g) Re-refining of Fats and Oils

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[19] D I Ashworth (to DeLaval Separator Co), U S Pat 2,157,882 (1939)
[20] W J Hund and L Rosenstein (to Shell Development Co), U S Pat 2,164,012 (1939)

Color of laboratory refined oil, 35 yellow, 10 9 red
Color of laboratory refined oil, re refined, 35 yellow, 9 3 red
Bleach color of above 20 yellow 2 7 red
Color of plant refined oil, 35 yellow, 13 5 red
Color of plant refined oil, re refined, 35 yellow, 9 8 red
Bleach color of above, 20 yellow 3 1 red

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acids The soapstock produced in centrifugal refining contains somewhat less fatty acids, due to less entrainment of neutral oil The usual fatty acid content of such soapstock is about 35% Soapstock produced by continuous soda ash refining usually contains not more than about 30% fatty acids That resulting from kettle refining by the wet method is variable in its content of fatty acids, but is never high

A few refiners process their kettle refined soapstock through centrifuges for the recovery of a certain proportion of low grade oil Such a process is of course impracticable in the case of soapstock produced by the more modern continuous methods Soapstock which is relatively high in fatty acids is often shipped from the refineries in tank cars without treatment, to be worked up into low grade soaps, or acidulated for the production of fatty acids In order to avoid freight charges for shipping excessive amounts of water, weak soapstocks are usually acidulated at the refinery, by boiling in lead lined tanks with dilute sulfuric acid The separated fatty acids are then shipped either to soapmakers or fatty acid distillers

5 Refining with Nonalkaline Reagents

Strong sulfuric acid has the power of dehydrating and precipitating mucilaginous materials, phosphatides, proteins, etc from fats and oils So called acid refining is carried out in lead lined tanks or other acid resistant tanks with concentrated sulfuric acid diluted with 10% to 20% of water The operation is not unlike alkali refining, *i e*, a small percentage of acid is run into the tank, the mixture is well agitated, and the impurities separate in the form of flocculent particles, which settle out of the clear oil Other acids, such as boric and phosphoric, have been patented for the purification of oils, but do not appear to have been used to any considerable extent · In most cases such acids are to be used in dilute solution, and it seems probable that purification results principally from hydration, rather than from strong dehydration and denaturation, as in sulfuric acid treatment

Acid refining is principally used in the treatment of linseed oil or other paint oils, to eliminate "break material" Only rarely is it used preliminary to alkali refining of edible oils, and then only in oils of extremely poor quality Low grade fats which are to be hydrolyzed by the Twitchell method are often given a preliminary acid treatment for the removal of substances which inhibit the action of the fat splitting catalyst

6. Solvent Refining

It has been proposed to remove fatty acids and other impurities from fats and oils by extracting the latter with solvents in which the impurities are soluble and the glycerides relatively insoluble Among the solvents

suggested for the purpose are alcohols[21] and furfural.[22] Equipment designed for the fractionation of oils by liquid–liquid extraction would also be suitable for solvent refining. Any large scale installation would presumably employ a packed column, or other column designed to produce intimate mixing of two liquids, in which the oil and solvent would circulate continuously in countercurrent flow. Means would of course have to be provided for distilling and recovering solvent from both the separated impurities and the purified oil. There are, so far as the author is aware, no commercial plants for carrying out solvent refining and it appears unlikely that the process could seriously compete with the newer continuous alkali refining processes as a general refining method.

Recently Hixson and Bockelmann[23] have demonstrated that liquid propane is an efficient solvent for the extraction of fatty acids from neutral oil, if employed at temperatures in the neighborhood of its critical pressure, and have published phase diagrams for the system propane–oleic acid–cottonseed oil. Pressures in the neighborhood of 600 pounds per square inch are required for the successful operation of this method of extraction. Propane and other normally gaseous hydrocarbons are used commercially for the treatment of lubricating oils, hence it is possible that in some cases they might prove practicable for the de-acidification of fatty oils. It seems probable, however, that propane extraction might prove more useful as a means of separating fatty acids from Twitchellized or other partially split fats than as a true refining method.

The caustic soda refining of crude oils in hydrocarbon solvents is said to proceed very satisfactorily. The loss of neutral oil incurred in ordinary alkali refining through the formation of emulsions is largely avoided; refining losses of most oils in a solvent medium are said to approach the Wesson loss closely.

7. Steam Refining

Steam refining, or the removal of free fatty acids from crude oils by steam distillation, is quite commonly practiced in Europe, but has never been much used in the United States. It is a highly effective method of treating certain types of oils and its relative unpopularity with American refiners may be attributed to the general lack of proper equipment for the operation and particularly the lack of means of heating batches of oil to high temperatures, rather than to shortcomings of the method itself.

[21] H. Bollman, U. S. Pat. 1,371,342 (1921).

[22] S. E. Freeman (to Pittsburgh Plate Glass Co.), U. S. Pats. 2,200,390 and 2,200,391 (1940). A. O. Tischer (to Eastman Kodak Co.), U. S. Pat. 2,090,738 (1937).

[23] A. W. Hixson and J. B. Bockelmann, *Trans. Am. Inst. Chem. Engrs.* 38, 891–930 (1942).

Steam refining is essentially similar, in both theory and practice, to steam deodorization, the principles of which are discussed at length in a later section. Although special equipment has been patented for de acidifying oils by steam distillation,[24] actually any efficient deodorizer, of either the batch or continuous type, will serve equally well for the purpose. Means must be provided for efficiently condensing and recovering the distilled acids. In order to attain a reasonably rapid rate of free fatty acid removal, it is essential to have some means of rapidly heating the crude oil to a minimum temperature of about 450°F. Dowtherm (diphenyl-diphenyl oxide) vapor heating systems are generally to be preferred over older systems, such as those involving direct firing or the circulation of mineral oils.

Since the rate at which fatty acids are distilled from an oil is directly proportional to their concentration in the oil, the substantial de acidification of an oil containing 2–10% of free acids requires a treatment not a great deal more severe than thorough deodorization. Thus, for example, the free fatty acid content of a 20,000 pound batch of palm oil may be reduced from 5.0% to 0.1% in about 2 hours, by treatment with steam at the rate of 300 pounds per hour, under a pressure of 0.25 inch, and at a temperature of 475°F. The loss under such circumstances will not exceed the percent fatty acids removed by more than about 1%, *i. e.*, in the above example will not be greater than about 6.0%. Data relative to the rate of fatty acid removal under different conditions, and the losses incurred in steam refining, will be found in the chapter on deodorization.

For certain purposes it may be feasible to reduce the free fatty acid content of the oil to a low figure, *e. g.*, below 0.1%, by steam distillation, and then finish its treatment by bleaching, or even by filtration without bleaching. A more common practice, however, is to reduce the free acids to 0.1–0.2% by distillation, and then give the oil a light caustic soda treatment to further reduce their concentration to 0.01–0.03%. The caustic treatment removes certain impurities other than fatty acids, and also shortens the time required for steam refining, since the lower concentrations of free fatty acids are the most difficult to remove by distillation. Theoretically, for example, it should require as much time or as much steam to reduce the free acids from 0.20% to 0.05% as from 2.0% to 0.5%. Actually, it requires somewhat more due to a slight tendency for the oil to hydrolyze and thus produce free acids, at the high temperatures employed in steam refining.

Steam refining is by no means a method of universal applicability, due to the tendency of some oils to darken when heated to high temperatures in the crude form. This tendency is particularly marked in the case of cottonseed oil, the color of this oil being easily "set" at a high temperature. On the other hand, some oils, such as palm oil, bleach under the influence of

[24] E. Wecker, U. S. Pat. 1,622,126 (1927).

heat Certain oils such as soybean oil and palm oil are inclined to break and deposit solid material in steam refining The formation of break material however does not necessarily interfere with the operation and it may usually be removed by filtration after refining is completed

Very prolonged steam treatment should be avoided when dealing with vegetable seed oils While it does not appear that the glycerides of such oils are appreciably damaged by long heating in the strict absence of oxygen the tocopherols and related substances which stabilize these oils against oxidation are more volatile than the glycerides and may be stripped out to a serious extent if distillation is long continued

8 Bleaching

The bleaching of fats and oils is almost invariably preceded by refining treatment which also effects some reduction in the color of the oil The object of bleaching is to remove coloring materials which are relatively unaffected by refining Such substances are almost without exception unobjectionable except insofar as they affect the appearance of the oil In some cases the preference of the consumer for light colored oils is entirely rational Thus for example the colors of light paints and enamels show to the best advantage only in a light colored oil vehicle In most cases however this preference rests simply upon the somewhat mistaken impression that color is a general index of purity and general high quality At any rate the preference of the consumer cannot be ignored and at the present time the production of light colored oils and fats is one of the primary concerns of manufacturers of both soaps and edible products

The processing treatments of refining hydrogenation and deodorization all have some incidental effect upon the color of oils but most fats and oils at some stage of processing are subjected to treatment designed exclusively to improve their color This treatment usually consists of bringing the oil into contact with a solid absorbent having an affinity for the coloring materials In practice the adsorbents used consist of bleaching clay (fuller s earth) and activated carbon Chemical methods are also used to some extent for bleaching They usually involve treatment of the oil with an oxidizing agent capable of oxidizing pigments to colorless forms Since such treatment also oxidizes and destroys antioxidants in the oil it is of limited applicability and is practically never used in connection with the manufacture of edible products Bleaching by means of an oxidizing current of air is in the same category with chemical bleaching methods

Bleaching is normally carried out after refining and prior to hydrogenation or deodorization as the lightest colored products are obtained by following this sequence of operations Some oils bleach only with great difficulty after exposure to high temperatures such as are employed in hydrogenation or deodorization Bleaching before hydrogenation is also

desirable because bleaching materials tend to adsorb traces of soaps and other catalyst poisons which may be left in the oil after refining

(a) *Methods of Color Measurement*

Among refiners in the United States the colors of the lighter refined and bleached oils, and also of shortenings and other oil and fat products, are usually determined by matching in a suitable tintometer a $5\frac{1}{4}$ inch column of the melted fat against red and yellow Lovibond color glasses The red glasses are standardized by the National Bureau of Standards in terms of the Priest Gibson N″ color scale[25] The N″ scale approximates, but does not exactly follow the scale adopted by the manufacturers of the glasses[26] The latter, incidentally, varies slightly from one set of glasses to the other Yellow glasses are not standardized, since relatively large variations in yellow are imperceptible to the eye, and in matching the color of a sample of oil it is only necessary to approximate the yellow color in order to obtain a satisfactory match with the red glasses

For most purposes, and in the case of most oils, the depth of color of the fat or oil is satisfactorily expressed in terms of red units, according to the above scheme The Lovibond system of color measurement is unsuitable, however, for oils which are excessively dark colored or which contain in considerable strength color elements other than red and yellow Among the vegetable oils which may contain colors other than red and yellow are olive oil, which generally has a greenish cast due to the presence of chlorophyll, and soybean oil, which may also contain considerable chlorophyll if expressed from green beans Oils obtained from damaged oil seeds are often brownish in color after refining, and hence are difficult or impossible to match with Lovibond glasses

Inedible tallows and greases are often too dark in color or too strong in green or other off colors to be graded in terms of the Lovibond system For the approximate evaluation of the colors of such fats, the Fat Analysis Committee of the American Oil Chemists' Society has provided an arbitrary system of color standards[27] consisting of sealed vials of solutions of various inorganic salts The color of any fat in question is determined by comparing a melted sample with the various standards until the nearest match is obtained The complete set of standards consists of 26 vials, numbered from 1 to 45, in odd numbers, and divided into five series Numbers 1 to 9, inclusive, are prepared for the grading of light-colored fats, numbers

[25] K S Gibson a[illegible] No 517 (1927)
K S Gibson and G [illegible] (1934),
Oil & Soap, 11, 246– [illegible] 167–178
(1935)

[26] I G Priest, *Oil & Fat Ind*, 6, No 9, 27–29 (1929)

[27] American Oil Chemists' Society, *Official and Tentative Methods* Revised to Jan 1, 1941 New Orleans 1941

11, 11 A, 11 B, and 11 C are for very yellow fats, numbers 13 to 19 are for dark, reddish fats, numbers 21 to 29 are for greenish fats, and numbers 31 to 45 are for very dark fats

The above so called FAC color system is somewhat confusing, inasmuch as the different series of standards are to some degree independent, and thus there is not an orderly increase in color from the lowest to the highest numbered members of the set Some of the standards numbered from 21 to 29, for example, may actually be lighter in color than standards numbered from 13 to 19 In addition, fats are often encountered which do not match any of the standards The FAC colors are of course not additive

A variety of systems are in vogue for evaluating the colors of paint and varnish oils All of these are described in detail by Gardner[28]

Obviously the only completely rational method of evaluating the color of an oil is by spectrophotometric analysis, whereby its absorption or transmittance is determined over the entire visible spectral range This method has the disadvantage, however, of requiring relatively complicated and expensive equipment, and of not yielding color values which, like Lovibond red units, can be expressed in terms of a single figure, and hence used in simple trading rules

(b) *Adsorbents Used in Bleaching Fats and Oils*

The most important adsorbent used in bleaching fats and oils is bleaching earth or clay Natural bleaching earth, otherwise known as fuller's earth, from its ancient use in the "fulling" or scouring of wool, comprises various earths or clays consisting basically of a hydrated aluminum silicate The mineralogical characteristics of these earths have been discussed by Kerr[29] and Nutting[30] Attempts have been made to correlate the chemical composition of earths with their bleaching ability, but without success An earth almost devoid of adsorptive capacity may be almost identical in composition with very active earth, hence these materials can be evaluated only by actual tests The earths used for bleaching fatty oils are the same as those used in a slightly different form and in much greater volume for the bleaching of petroleum products

Within recent years natural bleaching earths have for use with fats and oils been supplanted to a considerable degree by acid activated clays The raw materials used for the manufacture of this type of bleaching clay consist for the most part of bentonites which have little or no decolorizing power in the raw state[31] By treatment with sulfuric or hydrochloric acid,

[28] H A Gardner, *Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors*, 9th ed Inst Paint and Varnish Research, Washington, D C, 1939

[29] P F Kerr, *Am Mineral*, **17**, 192–198 (1932)

[30] P G Nutting, *U S Geol Survey Circ* **3**, 11, 17, 20 (1933)

[31] H Odeen and H D Slosson, *Oil & Soap*, **12**, 211–215 (1935)

however, the surface of the clay is so altered that its bleaching power will in most cases considerably exceed that of natural clays The acid treatment undoubtedly extends the surface of the clay, and probably also causes important changes in its chemical or physicochemical nature Acid activated clays retain more oil per unit weight of clay than do natural earths, but their use generally leads to a lower over all loss of oil through retention because of their greater activity

The activated clays are sold in neutral grades for bleaching edible oils and in slightly acid but more active grades, for difficultly bleachable inedible oils The former grades, like the natural earths, do not increase the free fatty acid content of the oils upon which they are used, whereas the latter are inclined to hydrolyze the oil slightly, increasing its free acid content by a few hundredths of a percent Although the higher cost per ton of activated earths is usually compensated by their greater activity and the lower over all loss of oil resulting from their use, so that they are often economical for bleaching ordinary high grade edible oils their greatest usefulness is in the treatment of off grade oils Certain types of color are extremely difficult to remove except by activated clays, *e g*, the green color due to chlorophyll in some soybean oils is much more responsive to a slightly acid earth than one of the ordinary type because of the instability of this pigment under acid conditions

Besides bleaching clay, the only adsorbent used to any extent on fatty oils is activated charcoal or carbon Because of its relatively high cost and its very high oil retention, carbon is not often used alone, but oil refiners very commonly employ it in admixture with bleaching clay, in a ratio of about 10 to 20 parts by weight of clay to 1 of carbon Such a mixture is considerably more effective than bleaching clay alone Carbon is very effective in removing the "bloom" caused by traces of mineral oil in vegetable oils, and is invariably used in the treatment of oils so contaminated The merest traces of mineral oil may increase the red color of an oil such as cottonseed oil by several Lovibond units The various grades of decolorizing carbon and their use are discussed at some length by Mantell[32]

(c) *The Pigments of Fats and Oils*

Although the pigments in fats and oils have been discussed in a previous chapter (pages 28–29), the nature and distribution of these substances in refined oils may well be briefly reviewed here

The reddish yellow color which is characteristic of most refined oils is due to various carotenoid pigments These pigments are readily adsorbed by bleaching earth or carbon, and in addition are to some extent either destroyed or converted to colorless or lighter colored forms by such process

[32] C L Mantell in J H Perry, *Chemical Engineers' Handbook* 2nd ed, McGraw Hill, New York, 1941

ing treatments as deodorization and hydrogenation Brownish pigments appear to be generally composed of degradation products of proteins, carbo hydrates, etc , and may be in the oil in the form of colloidal dispersions, rather than as true solutions The color of an oil containing such pig ments is often somewhat improved by careful clarification with the aid of diatomaceous earth or other material which has no adsorptive capacity for carotenoid pigments or other dissolved pigments Brown pigments do not often appear in oils of good quality, but may be found in large amounts in oils obtained from damaged materials They are in some cases exceed ingly difficult to remove

A greenish cast in an oil is generally due to chlorophyll Olive oil invariably contains some chlorophyll, and this pigment may also be found in soybean oil obtained from green beans, and in a few other minor seed oils Inedible tallow or grease may contain chlorophyll from accidental contamination of the fatty stock with the contents of the digestive tract of the slaughtered animals Chlorophyll may exist in the oil in different forms, not all of which are equally susceptible to ordinary bleaching treat ment In some cases a greenish oil may be readily bleached by the action of heat and bleaching earth, in other cases it may be very resistant to such treatment Treatment with alkali tends to render chlorophyll stable, whereas treatment with acids makes it unstable Consequently, most difficultly bleachable green oils are best processed by a light alkali treatment at a minimum temperature, followed by a heavy bleach with a slightly acid, activated earth Hydrogenation and deodorization have little effect upon such oils—hydrogenation, in fact, gives the appearance of intensifying the green color, through its bleaching action on the red and yellow pigments Hydrogenation also appears to affect chlorophyll chemically, in the case of soybean oil it causes the absorption maximum at 6600 Å to shift to about 6400 Å , corresponding to a conversion of α chlorophyll to β chlo rophyll

Oxidation has an important effect upon the color of fats and oils While oxidation bleaches the carotenoid pigments, it tends to develop the color of other types of coloring materials and in some cases apparently even produces colored compounds of a quinoid nature from the fatty acids or glycerides of the oil The partial oxidation of vegetable oils causes an increase in their red and yellow color, most of which is apparently due to formation of the chroman 5,6 quinones described by Golumbic [33] Cotton-seed oil is particularly prone to darken upon oxidation (Fig 60) Some lots of cottonseed oil darken so readily that the darkening tendency is noticeable in bleaching, poor bleach colors being obtained because of the development of new pigments parallel to the adsorption of old ones Such oil is also inclined to darken during deodorization Inedible animal fats

[33] C Golumbic, *J Am Chem Soc*, 64, 2337–2340 (1942)

of high free fatty acid content may become very dark colored through reaction of their free acids to form colored compounds Traces of iron and certain other metallic contaminants greatly favor the development of dark colors in such fats

It has long been known that the heating of unbleached oils to a high temperature may cause their color to become "set," after which they cannot be bleached It appears probable that oxidation is involved in this phenomenon, inasmuch as no such effect is observed in the case of oils which are hydrogenated or deodorized in an oxygen free atmosphere, after the removal of all dissolved oxygen

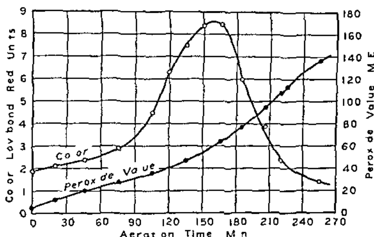


FIG 60 —Effect of oxidation on the color of refined and bleached cottonseed oil (oil aerated at 120°C)

(d) *The Theory of Bleaching by Adsorption*

Bleaching of oils by adsorption involves the removal of pigments which are either dissolved in the oil or present in the form of colloidally dispersed particles From the standpoint of adsorption theory, it is immaterial whether the pigments are dissolved or merely dispersed The mechanics of adsorption from such a system are somewhat controversial, there being some difference of opinion to the extent to which adsorption is physical and the extent to which it is a chemical phenomenon However, the mechanics of the process need not be discussed here at length It is sufficient to recall that adsorption is a surface phenomenon, depending upon a specific affinity between the solute and the adsorbent

The capacity of an adsorbent for a dissolved material is directly related to the concentration of the latter in the solution As the concentration of the solute decreases, there is a progressive and corresponding decrease in the amount of solute taken up by a unit weight of adsorbent The mathematical expression relating adsorption to residual solute concentration at

a single temperature was developed by Freundlich,[34] and may be stated as follows

$$x/m = Kc^n$$

where x = amount of substance adsorbed, m = amount of adsorbent, c = amount of residual substance, and K and n are constants The above equation may also be written in the form

$$\log x/m = \log K + n \log c$$

Thus it is apparent that a plot of x/m *vs* c on a log log scale will produce an adsorption isotherm which is a straight line, with a slope equal to n

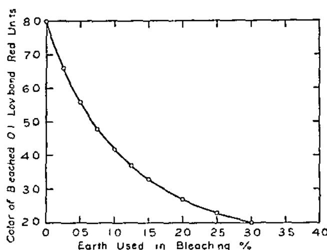


Fig 61 —Typical bleaching test on cottonseed oil (per cent earth used *vs* bleach color of oil)

Adsorption isotherms for a large variety of petroleum products are given by Rogers, Grimm, and Lemmon [35]

In the case of bleaching of fatty oils, the concentration of soluble coloring matter in the oil is usually expressed in terms of Lovibond or N″ red units The Freundlich equation is independent of the method of color measurement, so long as colors are expressed in additive units

Results of a typical test to determine the bleach colors produced by different percentages of an adsorbent are shown in Figure 61 In this test, the oil was a refined cottonseed oil with an initial red Lovibond color of 8 0 units, and the adsorbent was an acid activated bleaching clay The adsorp-

[34] H Freundlich, *Colloid & Capillary Chemistry* Translated from the 3rd German ed by H S Hatfield, Methuen, London, 1926

[35] T H Rogers, F V Grimm, and N E Lemmon, *Ind Eng Chem*, **18**, 164–169 (1926)

tion isotherm calculated from the results of the same test is reproduced in Figure 62 With x and c expressed in Lovibond red units, and m expressed as parts by weight of clay per 100 parts of oil, the value of K for this particular test was 1 17, and the value of n, 0 82

From a practical standpoint, K may be considered a general measure of the activity or decolorizing power of the adsorbent, whereas n is an indication of its characteristic manner of adsorption If two adsorbents have different capacities for adsorbing color, but adsorb in the same characteristic way, *i e*, if they exhibit different values for K, but the same value for n, the relative amounts required to effect a given degree of decolorization will be in inverse proportion to the values of K For ex-

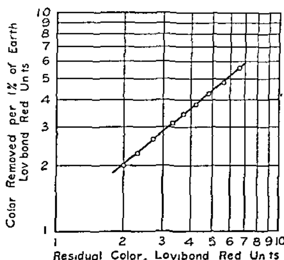


FIG 62 —Typical adsorption isotherm in the bleaching of cottonseed oil (same test as shown in Fig 61)

ample, if the following equations are found to apply to earths, A and B, respectively

$$(A) \qquad x/m = 0.5\, c^{0.5}$$

$$(B) \qquad x/m = 1.0\, c^{0.5}$$

bleaching with earth A will require twice as much earth as bleaching with earth B, and this relationship will hold at any level to which decolorization may be carried

The value of n determines the range of decolorization within which the adsorbent exhibits its greatest relative effect If n is high, the adsorbent will be relatively effective in removing the first portions of color from the oil, but relatively inefficient as an agent for effecting a very high degree of decolorization If n is low, the reverse will be true In comparing two adsorbents which yield markedly different values of n, it is thus important to specify the bleaching level at which the test is to be carried out It is

possible, for example, for adsorbent X to be superior to absorbent Y in bleaching refined cottonseed oil to a red color of 2 5, but for X to be inferior to Y in bleaching the same oil to a color of 1 0

Values of both K and n may vary widely, according to the nature of the oil, the nature of the adsorbent, and the method of bleaching In the laboratory bleaching of refined cottonseed oil with the official earth of the American Oil Chemists' Society, the values obtaining for K and n will be about 0 6 and 0 4, respectively This earth has a relatively low activity, however, even for a non acid treated product Comparable values of K and n for a good acid activated earth will be 1 0–1 2, and about 0 8, respectively The values of both K and n depend to a large degree upon the nature of the oil as well as that of the adsorbent Thus, for example, the data of Hassler and Hagberg[36] indicate the following approximate values for these constants

Refined cottonseed oil and fuller's earth, $K = 0\,6$, $n = 0\,45$
Crude coconut oil and fuller's earth $K = 0\,5$, $n = 1\,3$
Refined cottonseed oil and carbon, $K = 0\,20$, $n = 2\,2$
Crude coconut oil and carbon, $K = 7\,2$ $n = 1\,8$

Much more efficient bleaching is obtained in the plant than in the laboratory, which is apparently due to the fact that filtration of the oil from the earth is conducted under pressure in the plant, with a consequent shift in the equilibrium established between adsorbent and coloring materials Consequently, in plant practice, values of K will ordinarily be from 30% to 70% higher than in laboratory bleaching by the official A O C S method

It is evident from the Freundlich equation that bleaching clay or carbon which has reached equilibrium with respect to the coloring matter in a light oil will still have adsorptive capacity for the color in a darker oil In other words, the greatest efficiency of bleaching will theoretically be attained in countercurrent operation, in a system wherein fresh oil is treated only with used adsorbent, and fresh adsorbent is brought into contact only with oil that has been partially bleached True continuous countercurrent bleaching can be obtained if the adsorbent is in the form of relatively large lumps, as in the bleaching of petroleum products by percolation, but it can only be approximated if the bleaching material is in the form of a fine powder, as it is in the case of the clays and carbons used for the bleaching of fats and oils In the latter case, bleaching must be conducted in batches, but by using two or more separate bleaching kettles and filter presses, some of the advantages of the countercurrent method may be obtained Hassler and Hagberg[36] have reported results obtained in the bleaching of certain vegetable oils in two countercurrent stages

Multiple stage countercurrent bleaching is more advantageous at high

[36] J W Hassler and R A Hagberg, *Oil & Soap*, **16**, 188–191 (1939)

than at low values of n In spite of the theoretical advantages of this method of operation, it is seldom actually practiced

It can also be demonstrated, from the adsorption equation, that the application of an adsorbent in successive small portions should produce greater decolorization than the same amount of adsorbent applied in a single large dose As in the case of countercurrent bleaching, the advantages in this method of operation should theoretically increase with increase in the value of n However, Odeen and Slosson[31] have reported laboratory tests with acid activated clay in which multiple bleaching was less efficient than bleaching in which the entire amount of clay was added at one time It appears probable that the prolonged heating and aeration to which the oil is subjected in such tests either converts the pigments to a difficultly adsorbable form, or develops new color through the production of new pigments, or the darkening of those previously present

(e) *Adsorption Bleaching Methods*

Bleaching is usually carried out by the batch method, in kettles equipped with steam coils and medium speed agitators Since it is undesirable for the bleaching operation to be prolonged, bleaching kettles are in general somewhat smaller than the kettles used for refining, although of the same general design The kettles are preferably closed, so that they may be operated under vacuum, although open kettles are often used In operation, the kettles are charged with the oil to be bleached, the earth, or earth and carbon are added, and the batch is agitated while being heated to bleaching temperature Although there is a more or less common belief that the oil should be dried before the earth is added, it is reported by Odeen and Slosson[31] that this is unnecessary, or even undesirable The optimum temperature for bleaching varies somewhat with the oil and the adsorbent Vegetable oils are usually bleached at 220° to 240°F, while very dark colored inedible animal fats or palm oil may in some cases be bleached at a somewhat higher temperature Lard is bleached at a low temperature (160° to 180°F), with a very small amount of earth (usually not more than 0 5%), in order to avoid transmitting an "earthy" taste to the fat Activated earths are not ordinarily used on lard

After heating is completed, mixing is continued for a variable period, which is seldom longer than 20 to 30 minutes, and the batch is then pumped through a filter press The filtered oil is first returned to the bleaching kettle, and recirculation back to the kettle is continued until the color of the filtered oil reaches a minimum constant value Then the filtered oil is diverted to a separate tank, and filtration is completed The above method is applicable to reasonably well clarified oils If the oil contains much suspended matter, this should be removed by filtration, heating with salt and settling, etc, prior to bleaching, as some solid impurities are

adsorbed by bleaching clay or carbon, and thus reduce the bleaching capacity of these materials

Bleaching systems have also been devised in which the oil and adsorbent are mixed, heated, and separated by filtration in a continuous operation One of these[37] employs a device similar to those on large fire extinguishers of the "Foamite" type, for proportioning and mixing the bleaching earth and oil Oxidation of the oil is avoided by conducting all operations in a closed system, under vacuum, the oil being cooled to ordinary temperature through a heat exchanger before it is exposed to the atmosphere It is said that this system produces more efficient bleaching than batch systems, with less injury to the oil

Recently Mitchell and Kraybill[38] have demonstrated by means of ultraviolet absorption spectra that commercial bleaching commonly produces 0 1–0 2% of conjugated fatty acids in the glycerides of cottonseed, corn, soy bean, and linseed oils, through the isomerization of nonconjugated fatty acids Their observation is of some interest in its relation to the stability of bleached oils, in view of the readiness with which oxidation occurs in conjugated acids, and the autocatalytic nature of the oxidation reaction in fats Since some degree of prior oxidation was found to be prerequisite to this isomerization, it would seem that it might be maintained at a minimum by deaerating the oil before bleaching, and carrying out the bleaching under a vacuum Continuous vacuum bleaching should be particularly effective in inhibiting isomerization, since it presumably requires appreciable time, and the time of contact between earth and oil is much shorter in continuous bleaching than in bleaching by the batch system

Although no free fatty acids should be developed in bleaching an oil with a neutral or very slightly acid earth, a soapy oil may increase in free acid content by several hundredths of one per cent Odeen and Slosson[31] suggest that the clay decomposes the soap, adsorbing the sodium ion and leaving the fatty acid free In treating soapy oils they recommend heating the batch to 220°F , allowing it to stand for an hour or two, and then skimming off the surface layer of separated soap, before proceeding with the bleaching operation

In bleaching most oils the cost of the adsorbent is exceeded by that of the oil lost by retention in the spent adsorbent This oil is difficult to recover, and after recovery is invariably badly oxidized and of poor quality, hence many refineries discard their spent earth without treatment The retentiveness of an adsorbent is to some degree proportional to its activity, since both properties are related to the nature and extent of the adsorbing surface The less active fuller's earths may not retain more than 20–25% of their own weight of oil, but acid activated earths usually have a retention

[37] M M Jameson, *private communication to the author*

[38] J H Mitchell and H R Kraybill, *J Am Chem Soc* , 64, 988–994 (1942)

in the neighborhood of 40%.[39] Due to its very porous nature, carbon retains much greater amounts of oil than do any of the clays, and the addition of even 5% or 10% of carbon to a bleaching clay will materially increase the oil retention of the latter. The choice of an adsorbent depends in most cases upon striking a balance among the three factors of cost of the adsorbent, activity of the adsorbent, and oil retention. Although laboratory bleach tests and retention tests will give some indication of the value of a bleaching earth or carbon, it is necessary to resort to tests on a large scale to accurately evaluate these materials. The uncertainty in applying laboratory bleaching data to plant operations is in marked contrast to the utility of laboratory refining tests, which furnish a very reliable indication of the behavior of an oil in the plant.

The amount of adsorbent required for any given bleaching operation will vary greatly with the activity and nature of the adsorbent, the variety of oil, the color of the unbleached oil, and the color desired in the bleached oil. In general, however, the amounts of bleaching clay used vary from about 0.25% for lard, to about 5% for dark-colored inedible tallows and greases. Carbon is not often used to the extent of more than about 0.25%, and then usually in conjunction with bleaching clay. The data given previously in connection with the theory of adsorption furnish an indication of the amounts of earth required for bleaching refined vegetable oils.

(f) *Bleaching by Oxidation*

Some of the carotenoid pigments and possibly other coloring matters in fats and oils are converted to colorless or nearly colorless materials by oxidation. Consequently, bleaching by oxidation constitutes one of the available methods for producing light colored oils. Obviously it is impossible to oxidize the pigments in an oil without likewise oxidizing the glycerides of the oil to some extent, as well as destroying natural antioxidants. For this reason, bleaching by oxidation is of limited applicability. It is never employed in the treatment of edible fats, and its chief usefulness is in bleaching palm oil or dark-colored animal fats for soapmaking.

In some cases oils are bleached by means of atmospheric oxygen, the batch being simply blown with air for several hours at a moderately elevated temperature, *e.g.*, 150–200°F. Bleaching by aeration is particularly effective in the case of palm oil, since carotene is readily bleached by oxidation, and this oil is sufficiently low in iodine value for it to be possible to oxidize the pigments without oxidizing the oil itself to any advanced degree.

Most of the chemical agents which have been employed for bleaching are oxidizing agents. Among these, sodium dichromate is the one most

[39] For a laboratory method of evaluating the oil retention of bleaching earths see A. S. Richardson, J. T. R. Andrews, and R. G. Folzenlogen, *Oil & Fat Ind.*, 6, No. 9, 19–20, 43 (1929).

commonly used although the use of calcium and sodium hypochlorites and hydrogen peroxide has also been reported These reagents are usually used in a concentrated, strongly acid solution, hence lead lined or other acid resistant tanks are required for the operation The chrome bleaching of palm oil is described by Thomssen and Kemp[40] as follows If the oil contains an appreciable amount of settlings or solid material, these are first removed by boiling the charge with a 10% salt solution and wet steam, and allowing it to settle Bleaching is conducted in a lead lined tank, equipped with perforated coils for the injection of both steam and air The charge consists of one ton of oil The oil is brought to a temperature of 110°F, and 40 pounds of fine dry salt are sprinkled into the tank Then there are added 40 pounds of concentrated commercial hydrochloric acid and 17 pounds of sodium dichromate dissolved in 45 pounds of the same acid The latter solution is added slowly, over a period of about three hours, the charge is agitated with air during the addition of the dichromate solution, and for one hour thereafter At the end of this time, agitation is stopped and the aqueous phase is allowed to settle to the bottom of the tank, from which it is drawn off Water to the amount of 40 gallons is then added and the charge is agitated and heated with open steam to 150–160°F after which the operation is completed by allowing the contents of the tank to settle overnight

[40] E G Thomssen and C R Kemp *Modern Soap Making* MacNair Dorland Co New York, 1937, pp 30–32

CHAPTER XVII

DEODORIZATION

1 Introduction

Odorless and tasteless fats and oils first came into large demand as ingredients for margarine manufacture Carefully rendered beef and hog fats are relatively neutral in flavor, and such flavor as these fats do possess is sufficiently animal like in character as to be not too obtrusive in a butter substitute The natural flavors of the vegetable fats, however, are relatively strong, and in addition are utterly foreign to that of butter

In the latter part of the 19th century the demand for margarine fats in Europe grew to such proportions as to exceed the available supply of neutral animal fats It was natural, under such circumstances, that a means should have been sought for rendering vegetable fats sufficiently neutral to permit their incorporation into margarine

During the same period in which the new margarine industry was developing in northern and central Europe, there was a similarly rapid expansion in cotton production in the United States The growing of cotton on a large scale resulted in the production of large quantities of cottonseed oil In comparison with other vegetable oils, cottonseed oil is distinguished by an unusually high content of strongly flavored nonoil substances Even after alkali refining it is still so unpleasantly flavored as to be virtually inedible without deodorization Consequently, in order to make the American production of cottonseed oil available for edible purposes it was necessary from the beginning for the oil to be deodorized The first use of steam deodorization in the United States is attributed to Henry Eckstein The process was improved by David Wesson, who introduced the use of vacuum producing equipment in conjunction with steaming, and finally brought the process to its modern state of perfection by the combination of high vacua with high temperatures[1]

Margarine did not immediately become popular in the United States In fact, it is still relatively lacking in popularity throughout the Western Hemisphere Deodorized cottonseed oil was soon used on a huge scale, however, as an ingredient for lard substitutes or "shortenings," and to a lesser extent as a salad or cooking oil Large quantities of other vegetable oils, such as soybean and peanut oils, are now consumed in these products

[1] For a more detailed account of the history of deodorization see A P Lee and W G King, *Oil & Soap*, 14, 263–269 (1937)

The world production of deodorized oils and fats in the period 1935–1940 probably averaged between four and five billion pounds yearly

2. Nature of the Deodorization Process

Steam deodorization is feasible because of the great differences in volatility between the triglycerides and the substances which give oils and fats their natural flavors and odors It is essentially a process of steam distillation, wherein relatively volatile odoriferous and flavored substances are stripped from the relatively nonvolatile oil The operation is carried out at a high temperature to increase the volatility of the odoriferous components The application of reduced pressure during the operation protects the hot oil from atmospheric oxidation, prevents undue hydrolysis of the oil by the steam, and greatly reduces the quantity of steam required

Few of the compounds responsible for tastes and odors in oils have been individually identified Certain ketones, notably methyl nonyl ketone have been identified in coconut oil, palm kernel oil, and cocoa butter[2] Other common odoriferous components probably include aldehydes, hydrocarbons, and essential oils Flavor and odor removal is observed to generally parallel free fatty acid removal in oils Thus, for example, if an oil has an initial free fatty content of 0 10% the disappearance of noticeable flavor and odor will usually correspond to a reduction of the free fatty acid content to 0 02–0 04% It is probable, therefore, that the vapor pressures and molecular weights of the odoriferous substances are of the same order of magnitude as those of the common fatty acids of 12 to 18 carbon atoms

The concentration of odoriferous substances in an oil is generally quite low In the case of common oils such as cottonseed oil, peanut oil, soybean oil, tallow and lard, it does not appear to be greater than about 0 10% Hydrogenation of an oil imparts a decided flavor and odor This odor appears to be characteristic of the hydrogenation reaction, as it is similar for different varieties of oil, and is developed even in oils which have been thoroughly deodorized previous to hydrogenation

If deodorization is properly carried out, the removal of the odoriferous constituents from the oil is substantially complete Well deodorized oils of different kinds are indistinguishable from one another by odor or taste, and merely give a sensation of oiliness in the mouth

Deodorization also destroys any peroxides in the oil and removes any aldehydes or other volatile products which may have resulted from atmospheric oxidation However, strongly rancid oils cannot be completely reclaimed by deodorization, as such oils will have lost most of their natural antioxidants through oxidation, and hence will become rancid a second

[2] A Haller and A Lassieur, *Compt rend*, **160** 1013–1019 (1910), **151**, 697–699 (1911), A H Salway, *J Chem Soc*, **111**, 407–410 (1917)

time with relative ease Typical stability tests[3] on oil, before and after partial oxidation, and before and after deodorization of the partially oxidized products, are shown in Figure 63 Deodorization markedly reduces the color of vegetable oils, through its effect on their carotenoid pigments

Various methods other than steam deodorization have been proposed for rendering edible oils odorless and tasteless, but none, so far as the author is aware, have ever found commercial application In steam deodorization the stripping steam serves merely as a carrier for the substances to be distilled from the oil, and does not necessarily exert any chemical action on the oil Any other inert gas, such as hydrogen or nitrogen, would serve

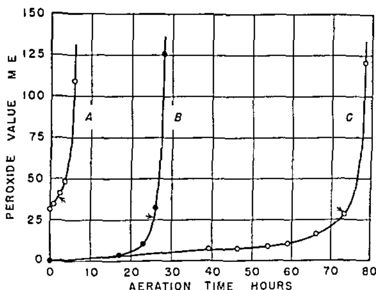


FIG 63 —Stability test curves (aeration at 110°C) of (C) hydrogenated peanut oil (A) the hydrogenated oil after oxidation to near rancidity, and (B) the oxidized *oil after steam deodorization Arrow indicates rancid point* [3]

equally well if it were as cheap as steam and if it could be condensed and thus easily removed from the deodorizer system

The free fatty acids of an oil are usually more or less completely removed by deodorization When the primary object is the removal of free acids, rather than flavor and odor, the process is termed "steam refining" The level to which the free fatty acid content of an oil can be reduced by deodorization is about the same as that produced by alkali refining, *i e*, about 0 01–0 02% Even under a high vacuum the stripping steam has a slight tendency to split the oil, with the formation of free acids The rate at which splitting occurs bears no relation to free acid concentration, at low levels of the latter On the other hand, the rate at which the free acids distill is directly proportional to their concentration in the oil Con-

[3] A E Bailey and R O Feuge, *Oil & Soap*, 21, 286–288 (1944)

sequently, as their concentration decreases, a point is eventually reached where the rate at which they are removed is equalled by the rate at which they are formed

3 Equipment for Batch Deodorization

Deodorization is usually carried out in closed, vertical, cylindrical steel vessels with conical or dished bottoms Deodorizers will occasionally be found with a capacity as high as 60,000 pounds, but a more usual capacity is somewhere between 15,000 and 30,000 pounds Oil at a temperature of 450°F (232°C) has a density of about 49 pounds per cubic foot, hence, a 20 000 pound deodorizer 8 feet in diameter will contain about 8 feet of oil at operating temperature

Injection of steam into the vessel while the latter is under vacuum results in considerable rolling and splashing of liquid so that approximately another 8 feet of headspace must be allowed between the oil level and the top of the vessel, to prevent oil from being entrained with the steam Spray separators of the centrifugal or louvre type are sometimes installed in the upper part of the vessel or in the vapor outlet pipe, although these are an unnecessary complication if there is adequate headspace above the oil

Vacuum for the deodorizer is almost invariably supplied by a multistage system of steam ejectors The primary thermocompressor of the system is preferably installed with the steam jets in a horizontal position directly over the vapor outlet at the top of the vessel (Fig 64) Lengthy or intricate piping between the deodorizer and the vacuum system is to be avoided, both because of the pressure drop in such pipes and the possibility of condensation and reflux of volatile materials to the deodorizer Because of the very large size of the vapor outlet lines, which are usually not less than 2 feet in diameter, the insertion of a vaportight valve in these lines is not generally considered practicable Both the deodorizer body and the vapor outlet should be well insulated

Some form of steam distributor must be provided in the bottom of the deodorizer for breaking up and distributing the flow of injected steam Various more or less elaborate steam dispersing devices have been patented, but these may be considered of more or less questionable value in view of evidence that high vaporization efficiency is attained in large deodorizers without their use The usual type of steam distributor, which appears to be quite satisfactory, consists of a simple flat "spider" consisting of 6 to 8 perforated pipes radiating from a central steam delivery line The perforations in the pipes should of course be properly related in combined cross sectional area to the cross sectional area of the pipes, so that the steam will discharge equally from all perforations

Some means of gaging and controlling the injected steam flow is neces-

sary An orifice type flowmeter may be used, but a simpler and equally satisfactory device consists of a rounded metering nozzle installed in the steam delivery line Valves are placed on either side of the nozzle, and compound pressure gages should be installed on either side of the nozzle between it and the valves The flow of steam from the mains through the first valve is easily adjusted to maintain steadily any desired pressure on the nozzle The steam flow through the nozzle will be proportional to the absolute pressure so long as the pressure on the delivery side of the nozzle is not more than 58% of that on the supply side As the pressure on the low side will usually be below atmospheric, that on the high side can be set at any desired value between about 10 to 20 pounds gage and the pressure prevailing in the steam mains As the latter will usually be 100 pounds or more, close regulation of the steam flow can be attained by making the nozzle of such size that the flow for the best operation is obtained at an intermediate value, of 60 to 75 pounds The proper size for the metering nozzle can be calculated from Grashof's formula, $w = 0.0165 Ap^{0.97}$, where w = flow of steam in pounds per second, A = cross sectional area of nozzle in square inches, and p = absolute steam pressure in pounds per square inch

Formerly, when vacua used in deodorization were low and injection steam requirements were correspondingly high, it was common practice to super heat the injected steam to prevent it from unduly cooling the batch of oil In modern installations which operate at a high vacuum and with very little injected steam, such a precaution is wholly unnecessary The sensible heat content of the steam is quite inconsequential in comparison with the heat capacity of the oil The steam will become superheated almost immediately upon contact with the oil and with insignificant abstraction of heat from the oil The wetness or dryness of the injected steam is like wise a matter of little consequence, but the steam should be substantially free from oxygen

Necessary accessories on the deodorizer include thermometers or thermo couples for measuring the temperature of the oil, and an accurate mercury filled manometer for measuring pressure on the vessel The manometer should be connected directly to the deodorizer body, above the surface of the oil, and should be of the closed-end type, so that it will indicate the absolute pressure on the deodorizer, rather than the difference between absolute and atmospheric pressure There will be sufficient barometric fluctuations from day to day to render an open manometer quite useless for the accurate measurement of high vacua

Oxygen is absorbed with the greatest readiness by oils at deodorizing temperatures, consequently it is of the greatest importance that the deodorizer and its fittings be free of air leaks It is preferable that it be of welded rather than of riveted or bolted construction

(a) *Equipment for Producing Vacuum*

As stated above, it is now practically universal practice to maintain vacuum on deodorizers by means of multiple stage steam ejectors For the best and most economical operation the vacuum equipment should be capable of maintaining an absolute pressure of not more than 0 25 inch (6 mm) of mercury Three stages of thermocompression are usually used, although some systems employ four or even five stages A three stage system of modern design, operating on steam at moderate pressures (100 to 150 pounds gage) and employing condenser water at ordinary tempera tures (60° to 80°F) will consume steam for compression equivalent to about 3 times the weight of the injected steam and will require a supply of condenser water equivalent to 40 to 50 times the weight of the total steam used for both injection and vacuum

Because of their simplicity and cheapness of construction and the fact that they have no surfaces to become fouled and require cleaning, inter-condensers of the barometric type are usually used in connection with the steam ejectors Where it is desirable to completely recover the materials distilled out of the oil, as in steam refining, the use of surface intercon densers may be advantageous, as with this type of condenser the volatile materials will not become mixed with the condenser water

Steam ejector vacuum equipment is not flexible in operation and for the greatest efficiency and economy it must be designed to maintain a definite pressure and handle a specific quantity of injected steam In order that deodorization may be conducted as rapidly as possible, it is desirable to inject steam at the maximum rate possible without undue entrainment of oil For deodorizers of 20,000 to 25 000 pounds capacity, 8 feet in diame ter, operating under a pressure of 0 25 inch, this rate will be in the neigh-borhood of 300 pounds of steam per hour

(b) *Heating the Oil for Deodorization*

It has been found in practice, and will also be evident from theoretical considerations to be discussed later, that temperatures of 425° to 475°F are required for rapid and complete deodorization As saturated steam must be generated at a gage pressure of about 315 pounds to attain a tem perature of 425°F , and about 530 pounds to attain a temperature of 475°F , ordinary steam boilers, operating at pressures of 150 to 200 pounds are not suitable for heating oil for deodorization

A number of different methods have been devised for heating the oil to a high temperature Because of the low ratio of surface to volume in vessels of large capacity it is not practicable to heat large deodorizers by direct firing A system has been considerably used, however, in which the batch of oil is heated by circulating it from the deodorizer through a system of tubes in an external furnace, the latter being heated by direct gas firing

Sufficiently high temperatures are attained by this method, but it has the serious disadvantage of subjecting portions of the oil to temperatures far above the actual temperatures required for deodorization Even with the most rapid and efficient circulation of oil through the tubes, the film of oil on the walls of the latter will reach a temperature greatly in excess of the average temperature of the circulating oil This effect is to some degree injurious to the product, and it also results in slow deposition of a coating of carbonized oil on the inside of the heating tube walls, necessitating periodic cleaning of the latter Other disadvantages are the difficulty of maintaining circulation of the hot oil with the complete elimination of "dead spots" in the heating zone, and the likelihood of seriously injuring the batch of oil in the event of the accidental breakdown of the circulating system

An alternative heating system which has also been widely used in the past utilizes a special, heat stable mineral oil as a heat transfer medium [4] The mineral oil is heated by direct gas firing, in a furnace similar to the one described above, and is circulated through heating pipes inside the deo dorizer In this system, as in the previous one, there are difficulties in maintaining rapid and turbulent flow throughout the heating zone There is moreover, a considerable tendency for even the most stable mineral oil to undergo decomposition in service A large amount of surface is required for heat transfer between the heating oil and the fatty oil, as the trans mission of heat from the former is much less efficient than that from a condensing vapor, is in heating with steam

Other methods which have been successfully used for attaining high oil temperatures for deodorizing include the use of special high pressure steam boilers, and steam compressors The use of superheated steam for heating oil to high temperatures is not practicable, as in this method only the rela tively slight sensible heat of the steam is available for heating the oil the latent heat of the steam of course not being available

A recently introduced system of heating for deodorization, which has proved eminently satisfactory in practice, is the so called 'Dowtherm" system [5] The essential element of this system is a specially designed liquid tube boiler, gas or oil fired, which vaporizes a mixture of diphenyl and diphenyl oxide (Dowtherm) The mixture, which consists of 26 5% di phenyl and 73 5% diphenyl oxide, is a eutetic which vaporizes without appreciable fractionation and has the advantage over either of its com ponents of having a relatively low melting point (53 6°F or 12°C)

Dowtherm boils at approximately 500°F (258°C) at atmospheric pres sure Consequently, vapors sufficiently high in temperature for heating oil

[4] See J P Harris and A B McKechnie *Oil & Fat Ind* , 4, 371–377 (1927)

[5] ' Dowtherm for High Temperature Heat Transfer Systems " Dow Chemical Co , Midland, 1940

TABLE 145
PROPERTIES OF SATURATED DOWTHERM VAPORS[a]

Temperature		Pressure		Heat content B t u /lb			Specific heat	Density lb /cu ft	
°F	°C	Lbs /sq in abs	Vacuum in Hg	Liquid	Latent	Total	Liquid	Liquid	Vapor
53 6	12 0			0	164	164	0 37		
60	15 6			2 4	163	165	0 38		
70	21 1			6 2	162	168	0 38		
80	26 7			10 1	161	171	0 39		
90	32 2			14 0	160	174	0 39		
100	37 8			18 0	158	176	0 40		
110	43 3			22 0	158	180	0 40		
120	48 9			26 0	157	183	0 40		
130	54 4			30 1	156	186	0 41		
140	60 0			34 2	155	189	0 41		
150	65 6			38 4	154	192	0 42		
160	71 1			42 6	154	197	0 42		
170	76 7			46 9	153 7	201	0 43		
180	82 2			51 2	152 0	203	0 43	63 1	
190	87 8			55 6	151	207	0 44	62 7	
200	93 3			60 0	150	210	0 44	62 5	0 0012
210	98 9			64 5	149	214	0 45	62 3	0 0016
220	104 5			69 0	148	217	0 45	61 9	0 0020
230	110	0 15	29 7	73 6	147	221	0 46	61 6	0 0030
240	115	0 20	29 6	78 2	146	224	0 46	61 4	0 0034
250	121	0 25	29 5	82 9	145	228	0 47	61 1	0 0045
260	127	0 29	29 4	87 7	144	232	0 48	60 8	0 0056
270	132	0 39	29 2	92 6	144	236	0 49	60 5	0 0070
280	137	0 49	29 0	97 5	143	240	0 49	60 1	0 0080
290	143	0 59	28 8	103 0	142	245	0 50	59 9	0 010
300	149	0 74	28 5	108 0	142	250	0 50	59 6	0 012
310	154	0 88	28 2	113 0	141	253	0 51	59 3	0 016
320	160	1 1	27 8	118 0	140	258	0 52	58 9	0 019
330	166	1 3	27 3	123 0	139	262	0 52	58 6	0 022
340	171	1 6	26 8	128 0	138	266	0 53	58 4	0 026
350	117	1 9	26 2	133 0	138	271	0 54	58 1	0 030
360	182	2 2	25 5	138 0	137	275	0 54	57 8	0 036
370	188	2 6	24 7	144 0	136	280	0 55	57 5	0 044
380	193	3 0	23 8	150 0	136	286	0 55	57 3	0 050
390	199	3 5	22 8	156 0	135	291	0 56	57 0	0 060
400	204	4 1	21 7	162 0	134	296	0 57	56 7	0 068
410	210	4 7	20 4	168 0	133	301	0 57	56 5	0 077
420	216	5 4	19 0	174 0	132	306	0 58	56 2	0 090
430	221	6 1	17 5	180 0	131	311	0 59	55 9	0 10
440	227	6 9	16 0	186 0	130	316	0 59	55 7	0 12
450	232	7 8	14 0	192 0	129	321	0 60	55 4	0 14
460	238	8 8	12 0	198 0	128	326	0 60	55 2	0 16
470	243	10	9 0	204 0	127	331	0 61	54 8	0 18
480	249	12	6 0	210 0	125	334	0 62	54 6	0 21
490	254	14	2 0	216 0	124	341	0 62	54 4	0 24

[a] From "Dowtherm for High Temperature Heat Transfer Systems" *Dow Chemical Co*, Midland, 1940

TABLE 145—*Concluded*

Temperature		Pressure		Heat content B t u /lb			Specific heat	Density lb /cu ft	
°F	°C	Lbs /sq in abs	Vacuum in Hg	Liquid	Latent	Total	Liquid	Liquid	Vapor
500	258	15	0 0	222 0	123	345	0 63	54 1	0 28
510	266	17	2 0	228 0	121	349	0 63	53 7	0 32
520	271	19	4 0	234 0	120	354	0 64	53 2	0 36
530	277	21	6 0	240 0	119	359	0 64	53 0	0 40
540	282	24	9 0	247 0	118	365	0 65	52 7	0 44
550	288	27	12	253 0	117	370	0 65	52 3	0 48
560	293	30	15	260	115	375	0 65	51 9	0 54
570	299	33	18	267 0	114	381	0 66	51 6	0 60
580	304	36	21	274 0	112	386	0 66	51 2	0 67
590	310	39	24	281 0	111	392	0 66	50 8	0 75
600	315	43	28	288 0	110	398	0 66	50 4	0 88
610	321	47	32	295 0	109	404	0 67	50 1	1 00
620	327	51	36	302 0	107	409	0 67	49 8	1 10
630	332	56	41	309 0	106	415	0 67	49 3	1 17
640	338	62	47	316 0	105	421	0 67	49 1	1 24
650	343	68	53	323 0	104	427	0 67	48 6	1 29
660	349	74	59	330 0	102	432	0 68	48 4	1 34
670	354	81	66	337 0	101	438	0 68	47 9	1 40
680	360	88	73	344 0	99	443	0 68	47 5	1 5
690	366	95	80	351 0	98	449	0 68	47 2	1 6
700	371	103	88	358 0	97	455	0 68	46 9	1 7
710	377	111	96	365 0	95	460	0 68	46 3	1 8
720	382	120	105	372 0	93	465	0 68	45 9	1 9
730	388	129	114	379 0	92	471	0 68	45 5	2 1
740	393	139	124	386 0	90	476	0 68	44 9	2 3
750	399	150	135	393 0	89	482	0 68	44 4	2 5

for deodorization can be generated at very low gage pressures (5 to 15 pounds) Thus, by substituting Dowtherm vapor heating for steam heating, it is possible to obtain all the advantages of heating by condensation of vapors without the trouble and expense involved in the use of high pressure equipment

Batch deodorizers are usually heated with Dowtherm by condensing vapors of the latter directly in heating coils inserted in the deodorizer, in exactly the same manner in which such vessels are ordinarily heated with steam Alternatively, the oil may be pumped to the deodorizer through a Dowtherm heated heat exchanger The Dowtherm system must, of course, be closed to prevent loss of vapors If there is an appreciable difference in elevation between the vapor generator and the deodorizers, the condensate from the latter may be simply returned to the generator by gravity, without the necessity of employing a circulating pump Deodorizers are generally installed at a considerable elevation, to permit the use of barometric condensers in conjunction with their vacuum equipment Due to the relative low latent heat per unit volume of Dow

therm vapor, somewhat larger heating coils and vapor passages are required than for steam

(c) *Cooling the Deodorized Oil*

A proper means for cooling the deodorized oil is a highly important part of the deodorization equipment, since it is essential that the oil be cooled to a low temperature before it is exposed to the air

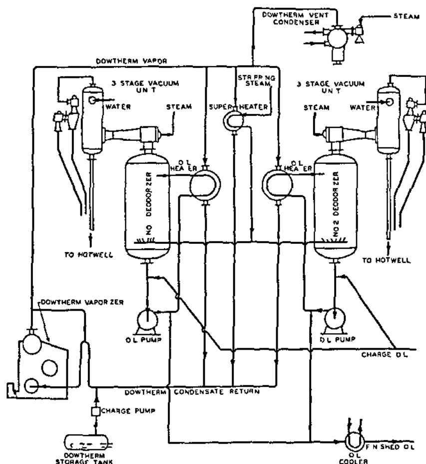


FIG 64—Dowtherm heating system employing external oil heaters for batch deodorizers (Courtesy *The Foster Wheeler Corp*)

Probably the most satisfactory method of operation is to cool the finished oil directly in the deodorizer while steaming is continued at a reduced rate to the very end of the cooling period This method has the advantage of avoiding the necessity of pumping hot oil, and of leaving the deodorizer cool after the charge is removed at the end of the operation It has the disadvantage of slowness and of sometimes requiring extra cooling coils in the deodorizer If cooling is to be conducted in a deodorizer which is heated by the circulation of hot mineral oil or Dowtherm, cooling water

of course cannot be used in the same coils as are used for heating The practice of discharging hot deodorized oil to separate evacuated tanks, and conducting the cooling operation in the latter is not to be recommended

If proper precautions are taken, the deodorized batch may be pumped directly out of the deodorizer while still hot, and cooled in a water to oil heat exchanger before it is discharged to the atmosphere Full vacuum must be maintained on the deodorizer during the pumping operation, and also steaming should preferably be continued Care should be exercised to insure that air is not drawn back into the deodorizer through the pump before the latter is fully primed After the batch is discharged, the empty, hot deodorizer should be immediately refilled with the next batch of oil Breaking of the vacuum on an empty deodorizer which is still hot will result in the formation of oxidized films of oil on the walls and coils of the vessel

An all steel centrifugal pump is usually used for discharging the oil The temperature of the cooled oil preferably should not be above about 120°F (49°C) in the case of salad and cooking oils and about 140°F (60°C) for hydrogenated shortenings

The importance of taking all possible precautions against oxidation of the hot oil after deodorization is completed can hardly be exaggerated Faulty operation in cooling the oil and removing it from the deodorizer can easily ruin the flavor and odor of an otherwise well deodorized product

4. Theoretical Considerations[6]

(a) *Theory of Steam Deodorization*

It may be assumed that oils and their associated volatile impurities conform to Raoult's law In other words, the vapor pressure of any volatile component in the oil may be assumed to be equal to its vapor pressure in pure form at the temperature in question multiplied by its molar concentration in the oil Mathematically

$$p_v = P_v\left(\frac{V}{O + V}\right) \qquad (1)$$

where p_v = equilibrium pressure of the volatile component in the oil, P_v = vapor pressure of the pure volatile component, V = moles of the volatile component, and O = moles of oil However, V is extremely small in relation to O, so that $O + V$ closely approaches the value of O Therefore, as a close approximation of equation (1) we may write

$$p_v = P_v \; V/O \qquad (2)$$

[6] See also the following W Brash, *J Soc Chem Ind*, **45**, 73–75, 331–333T (1926), A E Bailey, *Ind Eng Chem*, **33**, 404–408 (1941), H J Garber and F Lerman, *Trans Am Inst Chem Eng*, **39**, 113–131 (1943)

According to Dalton's law, in the vapors issuing from the deodorizer at any instant the molar ratio of volatile substance to steam will be the same as the corresponding ratio of their partial vapor pressures Mathematically

$$\frac{dS}{dV} = \frac{p_s}{p_v'} \tag{3}$$

where V = moles of volatile component, as before, S = moles of steam, p_s = actual partial pressure of the steam, and p_v' = actual partial pressure of the volatile component But p_v' is very small in comparison with p_s, so p_s closely approaches the total pressure Consequently as a close approximation of equation (3) we have

$$\frac{dS}{dO} = \frac{P}{p_v'} \tag{4}$$

where P = the total pressure, or $p_v' + p_s$

At this point a new factor, E, the vaporization efficiency, may be introduced By definition

$$E = \frac{p_v'}{p_v} \tag{5}$$

Combining equations (2) and (5)

$$p_v' = EP_v V/O \tag{6}$$

Finally, from equations (4) and (6)

$$\frac{dS}{dV} = \frac{PO}{EP_v V} \tag{7}$$

Integrating equation (7)

$$S = \frac{PO}{EP_v}\left(\ln \frac{V_1}{V_2}\right) \tag{8}$$

where V_1 = initial concentration of volatile substance in the oil, and V_2 = final concentration of volatile substance in the oil

The amount of steam required for deodorization (or the time required at a definite steaming rate) is thus seen to be (*a*) directly proportional to the size of the oil batch, (*b*) directly proportional to the absolute pressure in the deodorizer, (*c*) inversely proportional to the vapor pressure of the pure volatile or odoriferous components at the temperature of operation, (*d*) inversely proportional to the vaporization efficiency, and (*e*) directly proportional to the logarithm of the ratio of initial to final concentration of volatile substances

Practically speaking, the vaporization efficiency is a measure of the

completeness with which the steam becomes saturated with volatile substances during its passage through the oil From the two film theory of gas absorption of Whitman[7] it follows that at any instant the rate of transfer of volatile substance from the oil into a steam bubble is equal to the difference between saturation pressure in the bubble and actual pressure, times the surface area of the bubble, times a constant characteristic of the oil and the steam Mathematically

$$dp'_v/dt = kA(p_v - p'_v) \tag{9}$$

where t = time of contact between steam bubble and oil, A = surface area of the steam bubble, and k = gas diffusion constant

Integrating equation (9)

$$Akt = \ln\left(\frac{p_v}{p_v - p'_v}\right) \tag{10}$$

$$= \ln\left(\frac{1}{1 - \dfrac{p'_v}{p_v}}\right)$$

$$= \ln\frac{1}{1 - E} \tag{11}$$

$$\text{or} \quad E = 1 - e^{-Akt} \tag{12}$$

The vaporization efficiency thus increases with an extension of the total surface area of the steam bubble and with the time of contact between steam bubbles and oil

(b) Vaporization Efficiency

The magnitude of the vaporization efficiency actually attained in deodorization is of considerable practical importance because of its relation to possible improvements in deodorizer design It appears probable, from such experimental data as are available, that in ordinary practice it closely approaches the value of unity or, in other words, that the steam issuing from the deodorizer is very nearly saturated with volatile components

In a typical experiment[8] involving the removal of free fatty acids from acids from palm oil, the conditions of Table 146 were found to apply

If the various values recorded in this table are substituted in equation (8), using the mean vapor pressure of C_{16} and C_{18} acids as the vapor pressure of the pure volatile component, a calculated value for E of 0 82 is obtained Since the ratio of C_{16} to C_{18} acids in palm oil is approximately

[7] W G Whitman, *Chem & Met Eng*, 29, 146–148 (1923)

[8] A E Bailey, *Ind Eng Chem*, 33, 404–408 (1941)

2 to 3, and since the free acids of the original oil had been reduced from 4 6% to 2 6% by distillation before the experiment was started, it can be assumed that the average vapor pressure of the fatty acid mixture could hardly have been higher than the mean value of 22 5 mm Consequently, the value of 0 82 for the vaporization efficiency can be regarded as a minimum value

In view of the uncertainties involved in estimating the vapor pressure of the mixed acids, and other uncertainties inherent in conducting such tests in ordinary commercial equipment, no high order of precision can be claimed in the above calculation of vaporization efficiency, but the results seem to indicate that the efficiency is quite high In other experiments, calculated vaporization efficiencies varied from about 0 7 to 0 9

There is further confirmation of the view that vaporization efficiency is normally high in the fact that other experiments conducted at total pres-

TABLE 146

EXPERIMENTAL CONDITIONS IN THE REMOVAL OF FREE FATTY ACIDS FROM PALM OIL BY STEAM DISTILLATION[a]

Pounds of oil	19 000
Average molecular weight of oil	848
Moles of oil	22 4
Pounds of steam injected	200
Moles of steam	11 1
Temperature	460°F (238°C)
Absolute pressure, mm Hg	10
Initial free fatty acid content, %	2 6
Final free fatty acid content, %	0 9
Approximate vapor pressure of C_{16} acids at above temperature, mm [b]	30
Approximate vapor pressure of C_{18} acids at above temperature mm [b]	15
Mean vapor pressure C_{16} and C_{18} acids	22 5

[a] A E Bailey *Ind Eng Chem* **33**, 404–408 (1941)
[b] According to W O Pool and A W Ralston *Ind Eng Chem* **34**, 1104–1105 (1942)

sures varying from 6 to 25 mm yielded no correlation between pressure and calculated vaporization efficiency Theoretically the pressure should affect the efficiency considerably unless the latter is so high as to be close to unity at all pressures Eight and one half feet of oil in the deodorizer exerts a hydraulic pressure equivalent to about 190 mm of mercury Each bubble of steam during its passage through the oil is therefore subjected to a constantly varying external pressure, with a corresponding variation in its volume and area A high vacuum serves not only to make the average steam bubble comparatively large, thus making its surface area small in proportion to its volume, but also makes its average volume during its passage through the oil small in proportion to its final volume at the surface of the oil Vaporization efficiency is based upon instantaneous conditions

applying at the *surface* of the oil, therefore it should decrease as the vacuum increases That it apparently does not would indicate that saturation of the steam bubble at high temperatures is so rapid as to be substantially complete at any pressure down to at least 6 mm

(c) Losses in Deodorizing

In addition to the slight loss in weight occasioned by the removal of small quantities of odoriferous materials, there is also a small loss of neutral oil in deodorizing This oil is somewhat troublesome to recover from the condenser water if barometric condensers are used on the vacuum equipment, and will be badly contaminated with fatty acids and highly odoriferous material even if it is recovered Consequently it will either be lost entirely or diverted to very low grade uses Any oil carried out of the deodorizer represents a real loss, therefore, and the tendency for it to be carried out must be kept at a minimum

The principal source of oil loss in deodorizing is actual distillation of the triglycerides Although these materials are relatively nonvolatile (the vapor pressures of triglycerides are of the order of one thousandth that of their component fatty acids), they will nevertheless distill slightly at high temperatures The distillation losses in deodorizing hydrogenated cottonseed oil have been measured,[8] and found to be approximately 32 pounds per hour in the case of a 20,000 pound batch of oil, steamed at a rate of 350 pounds of steam per hour, under a pressure of 10 mm (Fig 65) As 1 to 1 5 hours of deodorization are required under these conditions to produce a well deodorized product, the distillation loss at 450°F will be seen to be in the neighborhood of 0 2% Losses at other temperatures will not be materially different, as the times required for deodorization will be in more of less inverse proportion to the ratio of distillation losses at the same temperatures The glycerides of low molecular weight of coconut type oils will distill at faster rates than those noted above This is to a considerable degree compensated, however, by the greater volatility of the odoriferous components of these oils and the consequent lack of necessity for deodorizing the oils for long periods or at very high temperatures

There is a very small and unavoidable loss resulting from hydrolysis of the oil by the steam, and consequent distillation of the fatty acids and glycerol The magnitude of this loss depends upon the vacuum under which deodorization is conducted It should not be greater than about 0 02–0 03% at a pressure of 0 25 inch and a temperature of 450°F, but may be somewhat greater at higher pressures

A third possible source of loss in deodorizing is mechanical entrainment of oil by the blowing steam Entrainment loss is negligible below a certain rate of steaming, but above this rate it increases very rapidly

Entrainment does not result from the oil's actually being thrown out of the deodorizer from the kinetic energy of the injected steam, but occurs rather when oil droplets thrown up above the surface of the oil are more powerfully impelled upward by the vapor stream than they are downward by the force of gravity The amount of entrainment occurring in any instance is thus related to the factors of velocity and density of the steam

Souders and Brown[9] have given the following expression for the critical velocity of vapor required for carrying droplets of a given size

$$v = KD^{\frac{1}{2}} \left(\frac{d_1 - d_2}{d_2} \right)^{\frac{1}{2}} \qquad (13)$$

where v = linear velocity of the vapor (steam), D = diameter of droplet, d_1 = density of droplet, d_2 = density of vapor, and K = a constant In

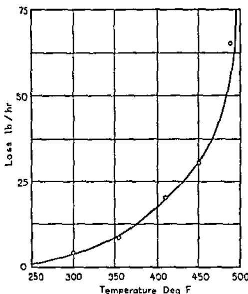


FIG 65 —Loss of neutral oil through distillation in batch deodorization [8]

this equation, the magnitude of d_2 is very small in relation to that of d_1 Consequently, as an approximation of equation (13) we may write

$$v = KD^{\frac{1}{2}} d^{\frac{1}{2}} (1/d_2^{\frac{1}{2}}) \qquad (14)$$

At a given temperature d_1 is constant, hence $d_1^{\frac{1}{2}}$ and K may be combined in a new constant K' Equation (14) then becomes

$$v = K' (D^{\frac{1}{2}}/d_2^{\frac{1}{2}}) \qquad (15)$$

It will thus be seen that the steam velocity required to entrain oil droplets varies with the square root of the diameter of the droplet The weight of

[9] M Souders and G G Brown, *Ind Eng Chem*, 26, 98–103 (1934)

the droplets, however, varies with the third power of the diameter There fore the weight of the largest droplets of oil that will be entrained varies with the sixth power of the steam velocity or flow The weight of the largest droplets does not, of course, correspond to the actual weight of oil entrained per unit time, but it is obvious that entrainment must in crease very rapidly with increase in the steam flow The data obtained by Bailey,[8] and which are shown graphically in Figure 66 illustrate the rapidity with which entrainment losses increase when the rate of steaming is carried to high levels

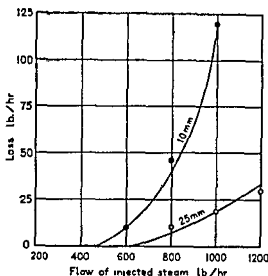


Fig 66 —Loss of oil through entrainment in batch deodorization [8]

(d) *Influence of Vacuum*

The amount of steam required for deodorization, as noted previously, is directly proportional to the absolute pressure Hence for the most eco nomical operation the vacuum should be as high as possible A pressure *of 0 25 inch (6 mm) or better is easily obtainable with well designed three* stage steam ejector equipment If, through the use of poor vacuum equip ment or poor operation of the equipment, a pressure no lower than 0 5 inch can be obtained, the steam requirements will be doubled, if a pressure no lower than 1 0 inch can be obtained, they will be quadrupled

The vacuum also has an important effect on the time required to complete the deodorization If, for example, steam is to be injected at a maximum rate of 350 pounds per hour at a pressure of 0 25 inch without excessive entrainment, it follows from equation (15) that the maximum permissible rate of steaming at a pressure of 1 0 inch is twice as great, or 700 pounds per hour *However, the weight of steam required for deodorization at* 1 0 inch is four times that required at 0 25 inch, hence twice as long will be required to deodorize at the higher pressure

The inhibiting effect of high vacuum on hydrolysis of the oil during deodorization is also somewhat important There are no very significant *differences in the loss of oil from hydrolysis at* different vacua, but even slight hydrolysis will make it difficult to obtain a low free fatty content in the finished deodorized oil In some cases the deodorization operation may be depended upon to effect a certain degree of refining of the oil For example, it may be desired to produce a finished oil with 0 01–0 03% of *free fatty acids from an oil* which initially contains 0 1–0 2% of acids If

the oil is being hydrolyzed during deodorization at the rate of 0 02–0 03% per hour, as it may be at 450°F under a pressure of 0 25 inch, a free fatty acid content of about 0 02% will be attained much more quickly than if the hourly rate of hydrolysis is 0 04–0 08%, as at a pressure of 0 5–1 0 inch The marked influence of pressure on the attainment of low free fatty acid contents in the oil is evident from Figure 67 A high vacuum in deodorizing is advantageous in every respect It leads to economy of operation, more rapid deodorization and a lower content of free fatty acids in the finished oil

(e) *Influence of Temperature*

The temperature at which deodorization is conducted has a very great effect upon the amount of steam required, and consequently the time consumed in the operation

It was noted previously that the steam requirements are inversely proportional to the vapor pressure of the pure volatile components of the oil, at the operating temperature According to the Clausius Clapeyron equation relating the vapor pressure of a substance to its temperature, the *logarithm* of the vapor pressure of the volatile constituents is within a limited range approximately proportional to its absolute temperature Thus if a given increment in temperature will double the volatility of the odoriferous substances, a further like increment will quadruple their volatility, etc

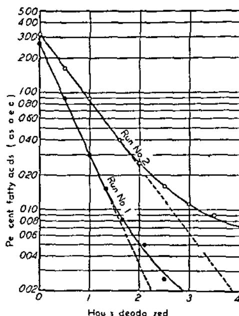


Fig 67 —Influence of vacuum on the

lbs steam per hour temperature 460°F 25 mm pressure

The rapid increase in vapor pressure which is caused by an increase in temperature is illustrated by the following values for the vapor pressure of palmitic acid at different temperatures[10] at 350°F, 1 8 mm, at 400° F, 7 4 mm, at 450°F, 25 mm, at 500°F, 72 mm The slope of the vapor pressure–temperature curves for volatile substances other than fatty acids

[10] W O Pool and A W Ralston *Ind Eng Chem*, 34, 1104–1105 (1942)

are unknown but it is unlikely that they are greatly different from thos palmitic and other fatty acids Thus by increasing the temperatur deodorization from 350°F (177°C) to 400°F (204°C), the rate at wl odoriferous substances are removed from the oil can be expected to proximately triple, and a further tripling in the rate can be expected raising the temperature to 450°F (232°C) Stated in another way, fo given standard of flavor and odor in the finished product about three ti as long will be required to deodorize at 350°F as at 400°F , and nine ti as long will be required as at 450°F

In actual operation the variation in time required for deodorization be found to be quite close to that predicted above

5. Deodorizer Design and Operation

(a) *Design of the Batch Deodorizer*

Numerous proposals have been made in the patent literature to emp deodorizing vessels of odd shapes and sizes, or with novel devices for est lishing contact between oil and steam The object has been to either i prove the efficiency of the process with respect to consumption of time steam, or to secure superior deodorized products

From the experience to date with deodorizers of unconventional desi and from the theoretical considerations mentioned previously, it does r appear likely that any form of batch deodorizer can be greatly, if at superior to the one customarily used

Deodorization is simply an adaption of the process of steam distillat and is governed by the well established principles of the latter Success deodorization depends upon nothing more than intelligently applying the principles and adequately protecting the oil from oxidation during t operation If this is done, the oil will be completely deprived of its od and flavor without injury to its stability or other desirable characteristi Once this goal is achieved, no further improvement in the product is po sible, and further improvements in the process are only possible in tl *direction of savings in time and expense of operation*

By operating at a temperature in the neighborhood of 475°F (246°C deodorization of large batches can be completed in one hour or less, opportunities for shortening the deodorization time are distinctly limite There is evidence, as stated previously, that in ordinary deodorizing practi the steam vapors leaving the deodorizer are substantially saturated wit volatile substances Therefore, it does not seem likely that steam co sumption can be much improved so long as the process is purely a batc operation Savings of steam are, however, possible by bringing the o and steam into contact in countercurrent streams, in a manner to be de scribed later

(b) Operation of the Batch Deodorizer

Deodorization, as stated previously, should always be conducted at the highest vacuum that it is possible to obtain The rate at which steam is injected will be related to the vacuum, since the steam ejector system will be designed to maintain a definite vacuum while compressing a specific flow of injected steam The ideal rate of flow is just below that at which entrainment becomes evident, this rate should of course never be even slightly exceeded

Where the equipment for heating the deodorizer permits a free choice of the temperature of operation, deodorization is usually conducted somewhere between 425° and 475°F (218° and 246°C) The optimum temperature for most products is probably nearer the latter than the former figure Most of the undesirable effects on the oil which have in the past been attributed to too high temperatures in deodorizing have in reality been due to oxidation, either from air leaks in the equipment or the use of oxygen containing steam Any effects of oxidation are greatly magnified at high temperatures

If the operation is conducted with rigid exclusion of oxygen from the oil, oils such as hydrogenated cottonseed oil can certainly be successfully deodorized at temperatures as high as 525°F (274°C) However, deodorization is so rapid at 475°F that there is perhaps little reason for exceeding this temperature Coconut oil, palm kernel oil, babassu oil and other oils containing large proportions of low molecular weight glycerides are usually deodorized either at temperatures somewhat lower than are used for other oils, or for a somewhat shorter time These oils are relatively easy to deodorize, and in addition their distillation losses are unduly high if deodorization is prolonged at high temperatures

Oils such as cottonseed oil can be much improved in flavor by deodorization for a limited time at a low temperature, *e g* , at 350°F (149°C) for 2 or 3 hours In fact much shortening and oil is so treated in the absence *of any source of heat for the deodorizers except low-pressure steam* Such products have a distinct residue of flavor and odor, however, and cannot be considered deodorized in the proper sense of the term

As stated previously, at any specified pressure and steaming rate, the time required for complete deodorization is in inverse ratio to the vapor pressure of the volatile components of the oil at the operating temperature Table 147 has been found a satisfactory guide for operation in the deodorization of cottonseed oil products It is based upon the vapor pressure of oleic acid, and assumes a steaming rate of 300 pounds per hour, a pressure of 0 25 inch, and a batch of 20,000 pounds of oil

If a molecular weight of 855 in the oil and a vaporization efficiency of 0 9 are assumed, it can be shown from equation (8) that deodorization

equivalent to that indicated in Table 147 should result in the free fatty acids of the oil being reduced to about *one tenth of their original value*. Due to hydrolysis of oil by the steam, however, the apparent removal of free acids will be somewhat less, if the latter are low (below about 0.5%) initially. Free fatty acids amounting to 0.1–0.2% should be reduced to 0.02–0.03%, however.

Some of the pigments of refined vegetable oils are bleached by high temperatures; consequently oils will normally be *somewhat lightened in color* by deodorization. The loss in color will depend somewhat upon the nature of the oil and the extent to which it has been subjected to previous bleaching treatments. Refined but unbleached cottonseed oil with a Lovibond red color of 7.0, for example, may come out of the deodorizer with a color of 3.0 to 5.0. However, shortening which has been treated with bleaching earth and carbon and further bleached by hydrogenation, to a red color of 1.5 to 2.5, may not lose more than 0.1 or 0.2 unit of red color in the deodorizer. Certain coloring matters of vegetable oils, and particularly cottonseed oil, are developed by limited oxidation.[11] At temperatures of 400°F. and above, their development seems to require very little oxygen, so that bleached and hydrogenated oils which are allowed to oxidize slightly in the deodorizer may actually increase in color.

TABLE 147
TIME REQUIRED FOR DEODORIZATION OF COTTONSEED OIL PRODUCTS[a]

Temperature		Vapor pressure of oleic acid, mm.	Time, hrs.
°F.	°C.		
350	177	1.4	16.0
375	191	2.5	9.0
400	204	4.6	4.9
425	218	8.3	2.7
450	232	15	1.5
475	246	25	0.9
500	260	43	0.5

[a] A. E. Bailey, *Ind. Eng. Chem.*, **33**, 404–408 (1941).

In deodorizing a batch of oil it is preferable to maintain a full vacuum on the deodorizer, and a flow of injected steam during practically the whole of the heating period. Steaming during the heating period serves to degas the oil before it has become extremely hot. If oil is heated to a high temperature before it is thoroughly stripped of dissolved oxygen, combination of the oil and oxygen will readily result, with injury to the color and stability of the product. After the batch has been raised to operating temperature, heating may usually be discontinued, as heat losses from a large, well insulated deodorizer will usually be insufficient to decrease the temperature

[11] C. Golumbic, *J. Am. Chem. Soc.*, **64**, 2337–2340 (1942).

more than 5° to 10°F during the remainder of the operation The precautions to be observed in cooling and removing the batch from the deodorizer have been outlined in a previous paragraph

After the deodorized oil is removed from the deodorizer it is usually filtered before being further processed, in order to insure perfect clarity in the finished product In some plants it is customary to also give the oil a light carbon treatment at this stage

Deodorization is invariably the final finishing step in processing an edible oil before it is filled into containers, made into margarine, or solidified and filled as a shortening The flavor of edible fat products is delicate and easily injured, after the oil has come out of the deodorizer it should be packaged as quickly as possible, and with a minimum amount of further heating, pumping, storage, or handling In the best managed plants edible oils are always packaged within a few hours, or even minutes, after leaving the deodorizer

6 Continuous Deodorization

Continuous systems for stripping fatty acids from oils by the use of steam have been in use for some time in Europe[12] Recently a continuous deodorizer for the production of high grade edible oils has been introduced into the United States[13]

In this apparatus (Fig 68), the oil flows downward in a tower fitted with trays and bubble caps, countercurrent to an ascending current of stripping steam The tower is constructed of stainless steel Vacuum is maintained on the tower by a three stage steam ejector system provided with barometric condensers A pressure of about 0 25 inch is maintained at the top of the tower, but there is a pressure gradient of about 0 75 inch from top to bottom, due to the constriction of the vapor stream at the bubble caps, and the hydraulic head of the oil in the trays Dowtherm vapor is used for heating the oil The apparatus is operated at substantially the same temperatures as are employed in batch deodorization

The advantages of countercurrent deodorization are analagous to those gained by any other countercurrent operation, including the common one of heat exchange In considering these advantages it is necessary to recall certain fundamental principles involved in the process The amount of volatile substances which the stripping steam will absorb before saturation is reached is a function of the concentration of these substances in the oil Thus in batch deodorization the steam carries a considerable content of volatiles during the first part of the operation, but in the latter stages the

[12] E Wecker, U S Pat 1,622 126 (1927)

[13] D K Dean (to Foster Wheeler Corp), U S Pat 2,280,896 (1942) D K Dean and E H Chapin *Oil & Soap*, **15**, 200–202 (1938) E H Chapin and D K Dean, *ibid* , **17**, 217–222 (1940)

stream will carry very little of these substances, because of their low concentration in the oil The steam leaving the deodorizer near the end of the operation may be saturated or nearly saturated with volatile material at the low concentration of the latter in the oil, and yet be capable of absorbing additional quantities of volatile substances from an undeodorized or partially deodorized oil Since the steam rising through the tower encounters successive layers of oil which are progressively richer in odoriferous

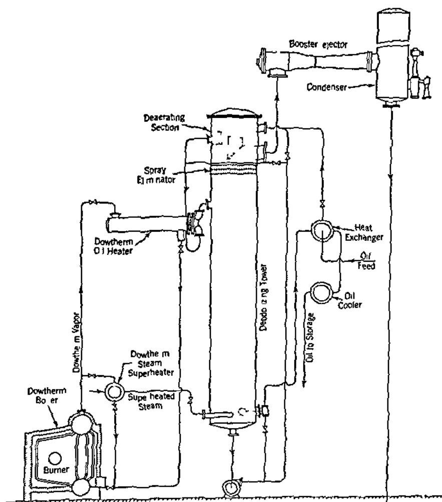


FIG 68 —Continuous deodorizing system (Courtesy *The Foster Wheeler Corp*)

constituents, and must finally pass through a layer of completely undeodorized oil before leaving the deodorizer, it continuously removes odors and flavors with the high efficiency encountered in batch deodorization only at the very beginning of the operation Thus a considerable saving in stripping steam is achieved, as compared with batch operation This saving extends also, of course, to the steam and water used for operation of the vacuum equipment It is also possible to effect some saving of heat by using the finished effluent oil to heat the raw incoming oil

In the first continuous deodorizers installed in the United States, no provision was made for eliminating dissolved air in the feed oil before the latter was heated to operating temperature This resulted in a slight oxidation of the oil, and resultant darkening and impairment in quality of the finished product In later designs of the apparatus this difficulty was eliminated by the installation of a deaerating chamber in the upper part of the tower The oil is passed through this chamber, which is under high vacuum, and is substantially degassed before it is heated to a high temperature

7 Steam Refining

The object in steam refining is to remove free fatty acids rather than odoriferous materials from the oil However, the techniques and the equipment used in steam refining are identical with those used for deodorization

The oils which can be successfully steam refined include coconut oil, peanut oil, sunflower oil, sesame oil and in fact, nearly all the commercially important oils with the exception of cottonseed oil Cottonseed oil contains certain pigments which darken when the oil is heated, and which cannot be subsequently removed by bleaching treatment It is usually desirable to reduce the free fatty acid content of the oil to a fairly low value, e g , to 0 1–0 2% by steam refining and then finish the oil by refining with alkali A somewhat better color will be obtained in the oil by this method than by straight steam refining However, for certain oils which are light colored in the crude form and relatively free of impurities, and particularly if the oils are to be later consumed as dark colored salad or cooking oils rather than in shortening or margarine, steam refining alone may prove adequate

Steam refining is particularly advantageous for oils which are relatively high in free fatty acids, and which consequently give high losses by alkali refining Palm oil for example cannot be refined with caustic soda without a very high refining loss whereas this oil can be refined by steam with a loss not greatly exceeding its free acid content

The time and steam required for reducing the free acid content of an oil from its original value to 0 1–0 2% can be calculated from equation (8) Below this content of free acids hydrolysis of the oil by the steam begins to become a noticeable factor, and this equation does not strictly apply It may be said in general, however that an oil with a free fatty acid content of 5 0% may be reduced to a free acid content of 0 10% in about 1 5 hours, by blowing with about 0 025 pound of steam per pound of oil, and to a free acid content of 0 03% in about 2 5 hours, with a stripping steam consumption of about 0 035 pound of steam per pound of oil These figures assume an operating temperature of 475°F and a pressure of 0 25 inch A further discussion of steam refining will be found on pages 519–521

CHAPTER XVIII

HYDROGENATION

1. Introduction

It is difficult to exaggerate the importance of the hydrogenation[1] process in modern oil and fat technology It is employed on a vast scale in both the soap and edible fat industries, for converting liquid oils to hard or plastic fats, for converting soft fats to firmer products, and for improving the resistance of fats and oils to deterioration through oxidation or flavor reversion To a far greater extent than any other process it has contributed to the present high degree of interchangeability amongst a wide variety of fats and oils The most obvious result of the introduction of hydrogenation on a wide scale has been the establishment of liquid oils, such as cottonseed and other vegetable seed oils, and marine oils, as adequate substitutes for originally more expensive hog and beef fats It is a mistake, however, to think of hydrogenation merely as a means of producing substitute products, inasmuch as hydrogenated fats may actually be superior in certain respects to any of the natural plastic fats In many instances, too, hydrogenation is now being employed to improve the consistency or stability of animal fats, as in the hydrogenation of lard or lard stearine, the hydrogenation of oleo oil for margarine manufacture, the hydrogenation of greases for soap making, etc

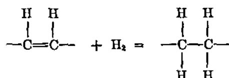
Although the hydrogenation of fatty oils was the first catalytic hydrogenation process to be adapted to commercial operation, and is yet by far the most important of such processes, there is singularly little known concerning its technology outside a relatively small group within the industry Of the voluminous literature on catalytic hydrogenation, only a minor portion is devoted to hydrogenation as applied to fats and oils, and most of this

[1] General References H Adkins, *Reactions of Hydrogen with Organic Compounds Over Copper Chromium Oxide and Nickel Catalysts* Univ of Wisconsin Press, Madison, 1937 S Berkman, J C Morrell, and G Egloff, *Catalysis*, Reinhold, New York, 1940 C Ellis, *Hydrogenation of Organic Substances*, 3rd ed , Van Nostrand New York, 1930 G Hefter and H Schonfeld, *Chemie und Technologie der Fette und Fettprodukte*, Vol II, Springer, Vienna 1939 T P Hilditch and C C Hall, *Catalytic Processes in Applied Chemistry* 2nd ed , Van Nostrand, New York, 1937 Natl Research Council, *Twelfth Report of the Committee on Contact Catalysis*, Wiley, New York, 1940 P Sabatier, *Catalysis in Organic Chemistry*, translated by E E Reid, Van Nostrand, New York, 1922 H S Taylor, *Industrial Hydrogen*, Chemical Catalog Co , New York, 1921

is so confused and contradictory as to be virtually worthless without benefit of expert and critical commentary. It is probably a fair estimate that 95% of the worthwhile literature on fat hydrogenation is unpublished, in the files of the firms actually engaged in manufacturing operations. The science has developed without free interchange of information amongst different workers, hence it is not surprising that practice varies widely from one manufacturing establishment to another. Because of the lack of an adequate literature, no presentation of the subject at this time can be considered comprehensive. However, the operations described in the ensuing portion of this chapter may be considered representative of good modern practice, if they are to be judged on the basis of the quality and characteristics of the hydrogenated products.

2. Nature of the Process

Hydrogenation of a fat consists simply in the direct addition of hydrogen at double bonds in the fatty acid chains, according to the following scheme:



Thus, the degree of hydrogenation in an oil is directly related to the iodine value, the addition of one mol of hydrogen corresponding to the absorption of one mol of iodine. In the case of fats of the average molecular weight of triolein, there theoretically are required 14.15 cubic feet of hydrogen at standard temperature and pressure, or about 16 cubic feet at ordinary temperature, to reduce the iodine value of 1000 pounds of oil 1 unit. On the basis of weight, this amounts to 0.0079% of hydrogen for each unit decrease in iodine value. Since fats are seldom hydrogenated to an extent corresponding to more than about 125 units decrease in iodine value, hydrogenation usually increases the weight of the oil less than 1%.

The catalyst employed in commercial hydrogenation invariably consists basically of nickel, although minor amounts of copper, alumina, etc., may be incorporated with the nickel for their "promoter" action. There has been some use of massive catalysts for continuous hydrogenation, but by far the greatest amount of hydrogenation is carried out with powder catalysts composed of the metal or metals in a finely divided form, prepared by special methods, and usually supported on a highly porous, inert, refractory material, such as kieselguhr. The catalyst is suspended in the oil during the operation of hydrogenation, and at the conclusion is removed by filtration. Although catalysts decrease in activity with repeated use, in most cases inactivation is slow, and a single charge of catalyst is ordinarily used a number of times.

For hydrogenation to take place, it is necessary to bring together at a suitable temperature, gaseous hydrogen, liquid oil, and the solid catalyst In ordinary practice it may be assumed that the hydrogen is first caused to dissolve in the oil, and the hydrogen-laden oil is then brought into contact with the catalyst by mechanical means In the usual type of equipment, the complete operation consists simply of agitating the suspension of catalyst and oil in a closed vessel in an atmosphere of hydrogen Agitation of the catalyst–oil mixture serves the double purpose of promoting solution of hydrogen in the oil, and continuously renewing the oil at the catalyst surface The solubility of hydrogen and other gases in oil, unlike their solubility in water, increases with increasing temperature, and of course is also increased by pressure

The rate at which hydrogenation will proceed under the conditions outlined above depends upon the temperature, the nature of the oil, the activity of the catalyst, the concentration of the catalyst, and the rate at which hydrogen and unsaturated oil molecules are supplied together to the active catalyst surface The composition and character of the hydrogenated product may vary according to the positions of the double bonds which are hydrogenated, as well as certain isomerizing influences accompanying the reaction, and are highly dependent upon the conditions of hydrogenation The influence of various factors on the rate and the course of the hydrogenation reaction will be considered in detail in later portions of this chapter

Although in the foregoing, mention has been made only of the hydrogenation of glycerides, the process is equally applicable to fatty acids, to nonglyceride esters, or to other fatty acid derivatives containing the original carbon to carbon double bonds

3. Theory of Heterogeneous Catalysis

A *catalyst, according to the classical definition* of Ostwald, is a substance which alters the rate of a chemical reaction, without affecting the energy factors of the reaction or being consumed in the reaction Properly speaking, therefore, a catalyst cannot initiate but can only accelerate a reaction However, in numerous instances, of which the hydrogenation of fats and oils is an example, reaction is so imperceptibly slow in the absence of a catalyst that the latter may for all practical purposes be considered an essential element of the reacting system

The permanent or self regenerative nature of catalysts is very important Although in the course of their action catalysts may enter into temporary combination with the reactants, such combinations are unstable and invariably are broken down at the completion of the reaction, to yield the catalyst in an unchanged form Thus the catalyst enters into the reaction over and over again, and a relatively small amount may be capable of

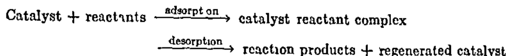
transforming very large amounts of material Ordinarily, the concentration of nickel employed as a catalyst for the hydrogenation of fats does not exceed a few hundredths of one percent of the weight of the fat

The fact that a catalyst cannot initiate reactions does not mean that the introduction of a catalyst into a reacting system may not influence the composition of the reaction products, or that different catalysts may not yield different products In many cases, reaction may follow a number of alternative courses, hence the composition of the final products will depend upon the relative rates of the various alternative reactions Where a number of different reactions occur together, the addition of a catalyst to the system may accelerate certain of these to a far greater extent than others Furthermore, one catalyst may differ from another in its relative effect on the different reaction rates The hydrogenation of fats and oils furnishes examples of such specificity of catalyst action Thus the addition of hydrogen to a linoleic acid chain in a glyceride molecule may yield either normal oleic acid or isomeric forms of this acid Some nickel catalysts are much more inclined than others to produce the isomeric forms

The type of catalysis which is the most important in industry, and the type which is operative in fat hydrogenation, is heterogeneous catalysis By definition, a heterogeneous system is one in which the catalyst and the reactants exist in different physical states Actually, such systems are in practice confined to those in which the catalyst is a solid and the reactants are liquids or gases Heterogeneous catalysis is to be somewhat sharply distinguished from homogeneous catalysis, in which the catalyst and the reactants comprise a single homogeneous phase In homogeneous catalysis the catalyst functions in the form of individual molecules, which are uniformly distributed throughout the reacting system Thus the question of catalyst structure, or of surface phenomena, does not enter into homogeneous catalysis On the other hand, in heterogeneous catalysis it is the catalyst surface which performs the catalytic function, hence the nature of the surface is of extreme importance A catalyst operating in a homogeneous system is defined simply in terms of its chemical constitution and its concentration in the system With all other factors controlled, the effect of a homogeneous catalyst of definite composition is exactly predictable upon the basis of its concentration However, if the catalyst is a solid, its behaviour will depend not only upon its chemical composition, but also to a very large degree upon both the extent and the nature of its surface The fact that the nature of a solid catalyst is determined so largely by the submicroscopic character of its surface renders the study and control of such catalysts very difficult Apparently similar catalysts may differ enormously in both their activity and their specific action

In heterogeneous catalysis it is now generally assumed that reaction proceeds through the formation of unstable intermediate compounds or

adsorption complexes, in which the catalyst is temporarily combined with one or more of the reactants If such compounds exist, it is probable that in most cases they are not definite chemical combinations, but consist merely of strongly bound molecules of the reactant which are held to the catalyst surface by secondary valence forces In any event, it is essential that they be unstable, i e, capable of being either decomposed or desorbed, to permit reaction to proceed according to the following scheme



Catalyst + reactants $\xrightarrow{\text{adsorption}}$ catalyst reactant complex

$\xrightarrow{\text{desorption}}$ reaction products + regenerated catalyst

Armstrong and Hilditch[2] postulated the formation of a hydrogen–nickel–unsaturated oil complex which breaks down to yield an oil of increased saturation and the free catalyst It has been suggested that hydrogenation with a metallic catalyst may be preceded by combination of the hydrogen with the catalyst to form metallic hydrides or metallic oxide hydrides

For molecules to react, their internal energy must first be raised above a critical level by the absorption of a certain quantity of energy from an external source This energy, known as the "energy of activation," is conceived graphically as being that required to raise the system to the top of a potential barrier opposing the reaction[3] Catalytic action is intimately related to the energy of activation, or in other words, to the height of this barrier

Modern views relative to the energy factor in catalysis have been reviewed by Berkman, Morrell, and Egloff[4] More recently, Grosse[5] has presented a simplified treatment of catalytic action from the standpoint of energy relationships The following explanation is derived from his article

The rate of a chemical reaction, k, is determined by the integrated Arrhenius equation

$$k = ae^{-E_{act}/RT}$$

where T is the absolute temperature, a is a factor related to the concentration of the reactants, and E_{act} represents the activation energy Due to the exponential character of the above equation, a relatively slight change in activation energy will have a large effect on the reaction rate Thus, for example, it is calculated that if the activation energy at 300°K is 50,000 calories, a 10% lowering of this energy requirement will increase the reaction rate 4400 times, whereas even a 1% lowering will increase it 2 3 times

[2] E F Armstrong and T P Hilditch *Proc Roy Soc London* **A98**, 27–40 (1920)

[3] H Eyring and M Polanyi *Z physik Chem* **B12**, 279–311 (1931)

[4] S Berkman, J C Morrell and G Egloff *Catalysis* Reinhold, New York, 1940

[5] A V Grosse *Ind Eng Chem* **35** 762–767 (1943)

Catalysts increase the reaction rate through their influence on the activation energy. A catalyst breaks the reaction up into two steps which are successively the combination of catalyst and reactants to form an unstable intermediate compound, and the breakdown of this compound, to yield a new product and the free catalyst. This has the effect of permitting the aforementioned barrier to be surmounted in two small steps, rather than one large one. Or in other words, two reactions with relatively low activation energies are substituted for a single reaction with a high activation energy. The alteration thus caused in the reaction rate is measured by the difference between the activation energy of the uncatalyzed reaction and that of the slower of the two steps of the catalyzed reaction. In view of the exponential relation outlined above, it is readily apparent that the catalyzed reaction may proceed at a rate which very greatly exceeds that of the uncatalyzed reaction.

4. Influence of Various Factors on the Course of Hydrogenation

(a) *Relation of Glyceride Structure to Hydrogenation*

The hydrogenation of fats and oils is greatly complicated by the mixed nature of the glycerides, and the fact that many fatty acids contain more than one double bond and hence can add hydrogen at more than one point along their chains. The diversity of courses which hydrogenation may follow may be appreciated by reference to Figure 69, which represents the double bond system of a glyceride molecule containing oleic, linoleic, and linolenic acid.

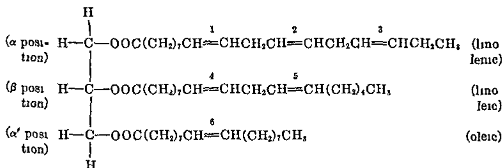


FIG. 69.—Double bond system of oleo linoleo linolenin.

Hydrogenation is ordinarily "selective," in the sense that hydrogen tends to add first to the most unsaturated acids. Thus the first addition of hydrogen to the molecule of Figure 69 would be expected to occur in the linolenic acid chain, to yield oleo dilinolein. However, selectivity is never complete and there is also the possibility of producing dioleo linolenin, through hydrogenation of the linoleic acid, or even stearo linoleo linolenin, through hydrogenation of the oleic acid. Similarly, a second addition of

hydrogen would be expected to take place in one of the two linoleic acid chains, to produce linoleo diolein However, it might take place in the oleic acid chain, to produce stearo dilinolein When it is recalled that any natural fat will consist of not one, but probably dozens of individual glycerides, each presenting different possibilities in the way of hydrogen addition, it may be seen that wide variation in the composition of the hydrogenated product may result from operation of the factor of selectivity alone

A second complication in the hydrogenation process arises from the circumstance that hydrogenation may occur alternatively in the α (outside) or β (inside) positions of unsaturated glycerides Referring again to Figure 69, if it is assumed that the first hydrogen molecule has added selectively at double bond No 3, to produce oleo dilinolein, two possibilities are presented for the selective addition of the second hydrogen molecule It may enter the linoleic acid radical which is in the α position, to produce β linoleo diolein, or it may combine with the linoleic acid radicle in the β position, to produce α linoleo diolein

The third complicating factor is the tendency of hydrogenation to form isomeric acids, with properties different from naturally occurring acids of a corresponding degree of unsaturation The readiness of a double bond to undergo hydrogenation varies inversely with its distance from the free end of the fatty acid chain, hence the double bonds of the linolenic acid in Figure 69 would tend to add hydrogen in the order 3, 2, 1, and those of the linoleic acid would tend to add hydrogen in the order 5, 4 Hydrogenation of the double bonds in this order would produce normal 9 10, 12 13 linoleic acid from linolenic acid, and normal 9 10 oleic acid from linoleic acid However, it invariably happens that there is some degree of hydrogenation in a contrary manner For example, hydrogenation of the 12 13 bond in linoleic acid to form normal 9 10 oleic acid is always accompanied by a minor amount of hydrogenation of the 9 10 double bond to form a positionally isomeric 12 13 acid Very little is known concerning positionally isomeric acids of hydrogenation with more than one double bond although such acids undoubtedly exist Toyama and Tsuchiya[6] have indicated the probable presence of solid (and hence isomeric) acids of two double bonds in hydrogenated sardine oil

Very recently, Lemon[6a] reported the presence in hydrogenated linseed oil of an isomeric linoleic acid which *does not* yield a conjugated system of double bonds upon alkali isomerization, and which may consequently be *presumed to be 9 10 15 16 octadecadienoic* acid produced by the addition of hydrogen at the 12 13 double bond of linolenic acid (bond 2 of Fig 69) In a typical experiment, the concentration of this isomeric acid reached a

[6] Y Toyama and T Tsuchiya, *J Soc Chem Ind Japan*, 28, 1079–1087 (1925)
[6a] H W Lemon *Can J Research*, F22, 191 198 (1944)

maximum of 18% of the total fatty acids at an iodine value of about 80, and thereafter declined, being very low at iodine values of 50 or below In oil hydrogenated to the consistency of shortening the concentration of the isomeric acid was about 13% The occurrence of this iso linoleic acid may have very great practical significance, as further experiments suggested very strongly that this acid is the compound specifically responsible for flavor reversion in hydrogenated linolenic acid oils

Apparently formation of solid isomers of oleic acid may occur both through hydrogenation of double bonds remote from the free end of the fatty acid chains, as outlined above, and also through both geometrical and positional isomerization of preformed oleic acid Thus, Moore,[7] Hilditch and Vidyarthi,[8] and others have observed the formation of elaidic acid, as well as 8 9, 10 11 and 11 12 oleic acids, in the hydrogenation of pure methyl and ethyl oleates However, it seems probable that the formation of high melting iso oleic acids chiefly occurs during the hydrogenation of linoleic acid since in practice such acids are chiefly produced in the early stages of hydrogenation during the time that the reaction is predominantly one of conversion of linoleic to oleic acid

The iso oleic acids are of concern to the practicing hydrogenator chiefly because of the influence of the higher melting members on the consistency of hydrogenated fats Hence the term "iso oleic acid," as commonly used, refers to the iso acids which have a higher melting point than normal oleic acid In other portions of this book, the term will thus be used in its popular sense Iso oleic acids yield lead soaps which are largely insoluble in cold alcohol or ether, hence they appear in varying proportions in the saturated acid fraction separated by methods of fractional crystallization, such as the ordinary Twitchell procedure Ordinarily, where the "iso oleic acid content" of a fat is reported, reference is made simply to the unsaturated acids found in the insoluble lead soaps

Although little or nothing is known of the properties of the liquid or low melting *iso oleic acids it appears reasonable to assume that these may* differ appreciably from normal oleic acid in certain properties, including possibly the readiness with which they undergo oxidation

The specific chemical individuals comprising the solid iso oleic acids have not been identified In some cases they may consist of *cis* acids in which the double bond is elsewhere than in the normal 9 10 position A 9 10 iso oleic acid can, of course, only be *trans* oleic (elaidic) acid In the case of the 12 13 acids or other acids in which the double bond is shifted toward the free end of the fatty acid chain, it is probable that only *trans* forms are involved, since in general the melting point of an acid is lowered as its double bond is so shifted

[7] C W Moore, *J Soc Chem Ind* 38, 320–325T (1919)
[8] T P Hilditch and N L Vidyarthi, *Proc Roy Soc London*, A122, 552–570 (1929)

Hydrogenation is not ordinarily considered to produce any rearrange nent of the fatty acid radicals within the glycerides Recently, however, Atherton and Hilditch[9] have reported a considerable degree of acyl wander ng in oils hydrogenated for prolonged periods at a relatively high tem erature (180°C), in the presence of an unstated concentration of nickel atalyst This phenomenon is presumably to some degree independent of actual hydrogenation, since it appears to occur to a slight extent in oil gitated with a nickel catalyst under an atmosphere of carbon dioxide

It is a matter of common experience in the industry that the operating ariables of the hydrogenation process, including temperature, pressure, tc , have a large influence on both the selectivity of the process and the mount of iso oleic acid formed, and that the latter in turn determine to a onsiderable extent the characteristics of the hydrogenated product It s probable that these variables also have some effect in determining the lirection of hydrogen to specific fatty acids in the glyceride molecule, as or example in determining whether hydrogen is added to acids in the α f β positions However, the inadequacy of present methods for the eluci lation of glyceride structure has so far precluded investigation of this eature of the process

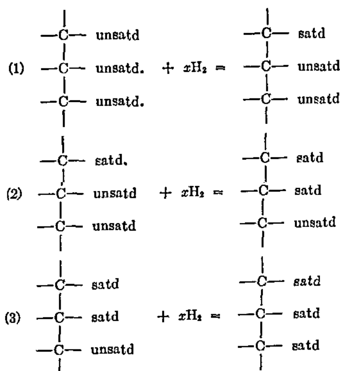


Fig 70 —Alternative course of hydrogenation in a mixture of glycerides of different egrees of unsaturation

Although hydrogenation tends to be selective in the sense that highly nsaturated fatty acids are hydrogenated more readily than less highly

[9] D Atherton and T P Hilditch *J Chem Soc* 1941 527–535

unsaturated acids, there is evidently much less selectivity with respect to the glycerides Bushell and Hilditch[10] have investigated this feature of the hydrogenation process, and concluded that triunsaturated glycerides hydrogenate somewhat more readily than diunsaturated glycerides, and that the latter, in turn are somewhat more easily reduced than mono unsaturated glycerides There is a considerable tendency, however, for hydrogenation of the two to occur simultaneously This tendency is illustrated by the results of their experiments in the hydrogenation of triolein A fat consisting originally of triolein should, if hydrogenated with perfect selectivity to an iodine value of 32, consist of no trisaturated glycerides 11 5% disaturated glycerides, and 88 5% monosaturated glycerides Actually, a sample of triolein hydrogenated to this iodine value was found to consist of 15% trisaturated 57% disaturated and 28% mono saturated glycerides

Contrary to the previous suggestions of Hilditch and Jones,[11] Bushell and Hilditch found that oleodipalmitin and oleodistearin hydrogenated with practically equal readiness, and that oleic acid in the α position in the glyceride molecules was hydrogenated no more readily than that in the β position

The lack of selectivity with respect to the hydrogenation of glycerides, quite as much as the equally unavoidable formation of iso acids, renders it impossible to produce hydrogenated fats or oils which are equivalent to some of the natural fats As shown by the researches of Hilditch and co-workers,[12] the saturated fatty acids in vegetable oils tend to be associated in the glyceride molecules with a maximum proportion of unsaturated fatty acids, so that there is a minimum content of highly saturated glycerides Consequently, these oils tend to be softer in consistency and lower in melting point than it is possible to make hydrogenated oils of the same iodine value Olive oil, for example, has an iodine value in the neighborhood of 80 but remains liquid down to quite low temperatures Soybean oil hydrogenated to this iodine value is lardlike in consistency at ordinary atmospheric temperature Animal fats, on the other hand, have their saturated fatty acids less evenly distributed, and hence can be approached quite closely in consistency by hydrogenated oils of equivalent iodine value Lard substitutes can be prepared by the hydrogenation of vegetable oils with iodine values in the same range as those of lard, *i e*, about 60 to 70

If two oils of different iodine value are to be hydrogenated to yield products of the same consistency, the more unsaturated oil cannot be hydrogenated to as low an iodine value as the less unsaturated oil Or stated somewhat differently, the further an oil is hydrogenated, the greater is its

[10] W J Bushell and T P Hilditch, *J Chem Soc*, 1937, 1767–1774
[11] T P Hilditch and E C Jones *J Chem Soc* 1932, 805–820
[12] T P Hilditch, *Chemical Constitution of Natural Fats* Wiley New York, 1941

deviation in character from natural oils Thus, for example, a shortening of the all hydrogenated type prepared from peanut oil may have an iodine value of 55 or lower, whereas similar shortenings made from cottonseed oil usually have iodine values greater than 60, and it is hardly possible to make such a shortening from soybean oil with an iodine value below about 70

Because of their highly unsaturated nature, marine oils present a somewhat distinctive problem in hydrogenation It has been shown by Richardson, Knuth, and Milligan,[13] and also by Hilditch and co workers,[14] that the highly unsaturated C_{20} and C_{22} acids of these oils do not hydrogenate with the same selectivity as the C_{16} and C_{18} acids of vegetable and land animal oils The high molecular weight fatty acids add hydrogen less readily than the C_{16} and C_{18} acids, and there is a tendency for the latter to become completely saturated even before the C_{20} and C_{22} acids are reduced to a single double bond Acids of high molecular weight appear generally to hydrogenate less readily than lower molecular weight acids of equivalent unsaturation Hilditch and Paul[15] have observed, for example, that erucic acid is hydrogenated with more difficulty than oleic acid

(b) *General Characteristics of the Hydrogenation Reaction*

Since the hydrogenation of an oil consists of not one but a series of reactions, it is hardly to be expected that any definite order can be assigned to the reaction as a whole On the other hand, it would be somewhat remarkable if the reaction rate bore no relation to the extent of unsaturation in the oil Actually, under most conditions, hydrogenation will approach the character of a monomolecular reaction, the rate of hydrogenation at any instant being roughly proportional to the unsaturation of the oil However, the character of the reaction is markedly influenced by various conditions of hydrogenation

A number of typical hydrogenation curves of cottonseed oil are reproduced in Figure 71, with the logarithm of the iodine value of the oil being plotted against hydrogenation time When so plotted a true monomolecular or first order reaction should yield a straight line, as in Curve *B* Curves similar to Curve *B* are often obtained under average conditions of pressure, agitation, and catalyst concentration at moderate or low temperatures, i e, below about 300°F At higher temperatures, the shape of the hydrogenation curve is more inclined to resemble Curve *C*, since an increase in temperature accelerates the first stages of hydrogenation to a

[13] A S Richardson, C A Knuth, and C H Milligan *Ind Eng Chem*, **17**, 80–83 (1925)
[14] T P Hilditch and J T Terleski *J Soc Chem Ind*, **56**, 315–322T (1937) D A Harper and T P Hilditch, *ibid* 322 329 (1937)
[15] T P Hilditch and H Paul, *J Soc Chem Ind*, **54**, 331–336T (1935)

relatively greater extent than the latter stages, *i e*, it accelerates the conversion of linoleic to oleic acid to a greater extent than the conversion of oleic to stearic acid In the case of Curve *A*, hydrogenation approaches a more nearly linear rate This type of curve is often obtained in the hydrogenation of relatively saturated oils, such as tallow, and is also observed in very rapid hydrogenation with a high concentration of catalyst, where the rate of hydrogenation is determined by the rate of solution of hydrogen *in the oil*

Curve *D* is characteristic of very high-temperature hydrogenation, of hydrogenation with a very low concentration of catalyst, or hydrogenation under conditions producing progressive slow poisoning of the catalyst during the reaction Curve *E* represents a hydrogenation carried out with a self poisoned nickel sulfate catalyst which was effective in the conversion

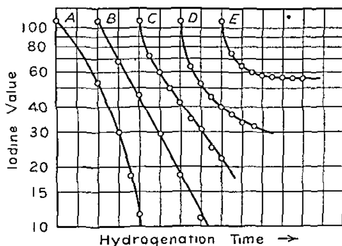


FIG 71 —Typical hydrogenation curves of cottonseed oil (iodine value *vs* hydrogenation time)

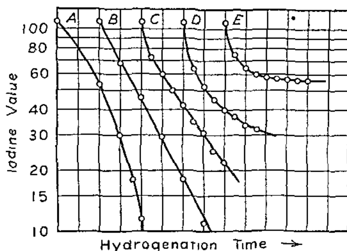
of linoleic acid, but almost completely ineffective for the hydrogenation of oleic acid Similar curves are obtained under conditions producing rapid catalyst poisoning

The course of hydrogenation, with respect to the fatty acid composition of the hydrogenated oil, is best shown with the aid of triangular diagrams, as first proposed by Moore, Richter, and Van Arsdel [16] Such a diagram is shown in Figure 72, which illustrates typical hydrogenations of cottonseed oil In a triangular diagram representing a three component system (in this case saturated acids, oleic acids, and linoleic acid) a mixture of any specific composition is indicated by a single point on the diagram In this case the fatty acid composition of the unhydrogenated cottonseed oil is

[16] H K Moore, G A Richter, and W B Van Arsdel, *J Ind Eng Chem*, 9, 451-462 (1917)

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[16] H K Moore G A Richter, and W B Van Arsdel, *J Ind Eng Chem*, 9, 451– (1917)

25% saturated acids, 25% oleic acid, and 50% linoleic acid Oil of this composition is indicated by the point A If hydrogenation were wholly selective, so that complete conversion of linoleic acid to oleic acid was obtained prior to any conversion of oleic to saturated (stearic) acid, hydrogenation would proceed along line AB to point B, and then along line BC to point C, at which point the oil would be completely saturated Similarly, wholly nonselective hydrogenation would proceed along lines AD and DC Partially selective hydrogenation is represented by any line proceeding from A to C through the area bounded by AB, BC, CD, and DA The selectivity of the process is measured by the closeness with which the hydrogenation curve approaches corner ABC

The actual course of hydrogenation, of cottonseed oil hydrogenated by the batch system, is represented by the typical curves, X and Y. Curve

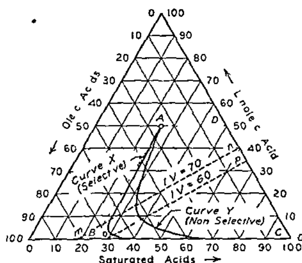


FIG 72 —Change in the composition of cottonseed oil during selective and non selective hydrogenation (typical hydrogenation curves)

X may be considered representative of quite selective hydrogenation, whereas Curve Y represents hydrogenation decidedly lacking in selectivity Practically all commercial products will be found to be intermediate in composition between X and Y However, it is possible to hydrogenate slightly more selectively and considerably more nonselectively in the laboratory under somewhat extreme conditions of temperature, pressure, agitation, catalyst concentration, etc

Products having iodine values of 70 and 60, respectively, are represented in Figure 72 by the lines mn and op A comparison of the composition of products X and Y at these two iodine values is presented in Table 148

In the case of other oleic linoleic acid oils, such as peanut oil, soybean oil, sesame oil, corn oil, sunflower oil, etc , hydrogenation follows a course similar to that of cottonseed oil However, it is to be remembered that all

of these oils contain less saturated acids than cottonseed oil, hence they will be inclined to contain less saturated acids, more oleic acids, and less linoleic acid after hydrogenation to any given iodine value In the case of soybean, corn, and sunflower oils, this is not to be construed as meaning that hydrogenated products of equivalent iodine value will be softer than hydrogenated cottonseed oil Insofar as the consistency of the products is concerned, the lesser content of saturated fatty acids in these hydro-

TABLE 148

COMPOSITION OF SELECTIVELY AND NONSELECTIVELY HYDROGENATED COTTONSEED OIL AT IODINE VALUES OF 70 AND 60

Hydrogenation conditions	Iodine values	Percentage composition of fatty acids		
		Saturated	Oleic	Linoleic
Selective	70	27 0	65 0	8 0
Nonselective	70	33 5	52 0	14 5
Selective	60	31 5	67 0	1 5
Nonselective	60	38 5	52 5	8 5

TABLE 149

COMPARISON BETWEEN COTTONSEED OIL AND PEANUT OIL HYDROGENATED UNDER IDENTICAL CONDITIONS TO AN IODINE VALUE OF 65

Oil	Hydrogenation conditions	Percentage composition of fatty acids		
		Saturated	Oleic	Linoleic
Cottonseed	Moderately selective	31 5	64 5	4 0
Peanut	Moderately selective	27 5	72 5	nil
Cottonseed	Nonselective	36 0	56 0	8 0
Peanut	Nonselective	30 0	67 0	3 0
Cottonseed	Very nonselective	39 5	48 5	12 0
Peanut	Very nonselective	33 0	61 0	6 0

genated oils will be more than counterbalanced by greater contents of both fully saturated glycerides and iso oleic acids

The data of Table 149 furnish an idea of the differences in composition between cottonseed oil and peanut oil hydrogenated under identical conditions to a common iodine value

In all of the preceding discussion, reference has been made only to "oleic acids," and no distinction has been made between normal oleic and iso-oleic acids formed during hydrogenation In the course of hydrogenation, the content of iso oleic acid approaches a maximum value at a more or

less linear rate, and thereafter declines The iodine value at which the maximum value is attained is somewhat variable, but in the case of hydrogenated cottonseed oil it is generally between about 45 and 55 However, there is usually but a slight increase in iso oleic acid after an iodine value of about 65 to 60 is reached The maximum amount of iso oleic acid formed will vary greatly with hydrogenation conditions It may be as low as 10%, or less, or as great as 30%, or more Typical plots of iodine value *vs* iso oleic acid content, for hydrogenated cottonseed oil are shown in Figure 73

Both selectivity and iso oleic acid formation are markedly influenced by operating variables in the hydrogenation process, which in the case of ordinary batch hydrogenation with a powder catalyst, include temperature, hydrogen pressure, agitation, catalyst concentration, and the nature

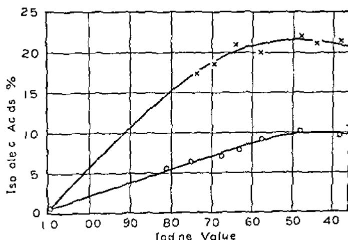


FIG 73 —Formation of iso oleic acids during the hydrogenation of cottonseed oil (typical runs involving good and poor repression of iso oleic acid)

of the catalyst The effect of these variables on the hydrogenation of oleic linoleic acid oils has been the subject of a considerable amount of investigation Among the more extensive investigations reported may be mentioned those of Moore Richter, and Van Arsdel,[16] Richardson, Knuth, and Milligan,[17] Dhingra Hilditch, and Rhead,[18] and Bailey, Feuge, and Smith [19]

As stated previously, the present lack of reliable methods for estimating individual glycerides, or even most classes of glycerides, makes it impossible to follow the course of hydrogenation in terms of glycerides rather

[17] A S Richardson C A Knuth, and C H Milligan *Ind Eng Chem* , **16**, 519 522 (1924)

[18] D R Dhingra, T P Hilditch, and A J Rhead, *J Soc Chem Ind* , **51**, 195–198T (1932)

[19] A E Bailey, R O Feuge, and B A Smith, *Oil & Soap*, **19**, 169–176 (1942)

than fatty acids However, the Hilditch technique for the estimation of fully saturated glycerides affords a reasonably satisfactory means for determining the increase in this particular class of glycerides as hydrogenation proceeds Hilditch and co workers have examined a number of fats during the course of hydrogenation, with respect to their fully saturated glyceride content The data of Hilditch and Jones[11] on hydrogenated cottonseed oil are of particular interest The curve of Figure 74 is constructed from the data of the latter authors

(c) *Influence of Temperature*

Catalytic hydrogenation, like other chemical reactions, is accelerated by an increase in temperature However, the effect of temperature on the reaction rate is somewhat less than in ordinary chemical reactions in a

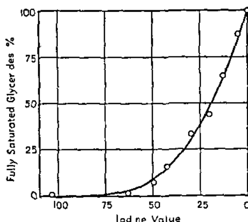


FIG 74—Formation of fully saturated glycerides during the hydrogenation of cottonseed oil (according to the data of Hilditch and Jones)

homogeneous system, and is also variable Under most conditions, within the temperature interval of about 120° to 300°F, the time for hydrogenation to a given iodine value will be about halved by raising the temperature 35° to 45°F These figures are to be regarded as only very roughly approximate however, since the effect of temperature is different under different hydrogenation conditions, and with different oils In fact, comparisons made with the same oil under like conditions will reveal different results, according to the degree of hydrogenation chosen for comparison At temperatures above about 350° to 360°F the effect of increasing the temperature is much less, and a maximum reaction velocity is reached at 400° to 425°F, after which further increase in the temperature may actually decrease the rate of hydrogenation

Over the ordinary range of hydrogenation temperatures, increasing the temperature has a relatively greater effect upon the conversion of linoleic

to oleic acid than upon the conversion of oleic to stearic acid Hence, selectivity is enhanced by increasing the temperature The temperature at which hydrogenation is carried out also has a marked influence upon the formation of iso oleic acids, greater quantities of these acids being produced at higher temperatures The data of Table 150 illustrate the effect of temperature on the composition of cottonseed oil hydrogenated under constant conditions of pressure, agitation, catalyst concentration, etc

(d) Influence of Pressure and Agitation

Since hydrogen must first become dissolved in the oil before it can reach the catalyst–oil interface where hydrogenation occurs, any factor influencing the rate of solution will have a corresponding effect on the rate of hydrogenation The factors specifically affecting rate of solution are pressure of the hydrogen and degree of agitation of the catalyst–oil charge

TABLE 150

COMPARISON OF COTTONSEED OIL SAMPLES HYDROGENATED TO AN IODINE VALUE OF 62 9 AT DIFFERENT TEMPERATURES BUT WITH OTHER CONDITIONS OF HYDROGENATION CONSTANT (LABORATORY HYDROGENATIONS)[a]

Run No	Temp °F	Catalyst concentration % nickel	Hydrogenation time min	Percentage composition of fatty acids			
				Satd	Iso-oleic	Oleic	Linoleic
20	250	0 05	72	39 6	8 5	39 3	12 6
12	300	0 05	31	34 1	11 2	47 5	7 2
18	350	0 05	19	32 5	14 3	47 6	5 6
Composition of oil before hydrogenation				26 9	—	27 1	46 0

[a] A E Bailey, R O Feuge, and B A Smith, *Oil & Soap*, 19, 169–176 (1942)

Within the range of pressure of ordinary commercial hydrogenation, *i e*, about 1 to 6 atmospheres, or up to about 75 pounds gage pressure, the hydrogenation rate is inclined to be roughly proportional to the absolute pressure The factor of agitation is difficult, if not impossible to evaluate quantitatively, although large differences in reaction rates may be produced by varying the agitation Theoretically, agitation of the oil in a batch hydrogenator serves two purposes It produces a relative motion of oil and catalyst particles, thus continually renewing the oil at the catalyst surface, and it extends the hydrogen–oil interface, presenting an increased surface for diffusion of the gas into the oil

From the behavior of hydrogenated oils in practice it appears that the reaction rate is largely controlled by the magnitude of the surface presented by the oil to the hydrogen, rather than the degree to which mixing is attained between catalyst particles and oil Hence, in commercial systems

the chief object sought is efficient contact between hydrogen and oil In batch hydrogenation the size of the reactor has an important bearing upon the attainable degree of agitation As explained above, the agitation obtained in a hydrogenation apparatus is measured by the average interface maintained between hydrogen and oil while the apparatus is in operation This interface exists in two dimensions, hence its magnitude is a function of the second power of the diameter, depth, or other linear dimension of the apparatus On the other hand, the size of the oil charge is a function of the third power of this dimension In equipment of a given design therefore, it is impossible to obtain as good agitation in large as in small units As a result of this circumstance, it is unfortunately not possible to directly compare small-scale laboratory hydrogenation experiments and large-scale plant operations Ordinarily, the agitation in a laboratory

TABLE 151

COMPARISON OF COTTONSEED OIL SAMPLES HYDROGENATED TO AN IODINE VALUE OF 62 9 AT DIFFERENT PRESSURES BUT WITH OTHER HYDROGENATION CONDITIONS CONSTANT, AND HYDROGENATED WITH DIFFERENT DEGREES OF AGITATION, BUT WITH OTHER CONDITIONS CONSTANT (LABORATORY HYDROGENATIONS)[a]

Run No	Pressure lbs /sq in gage	Agitation		Catalyst concn % nickel	Hydrogenation time min	Percentage composition of fatty acids			
		R p.m	Lbs oil			Satd	Iso-oleic	Oleic	Linoleic
19	5	408	12	0 05	67	32 8	13 2	48 1	5 9
12	27	408	12	0 05	31	34 1	11 2	47 5	7 2
17	50	408	12	0 05	21	35 2	10 2	46 2	8 4
11	27	290	16	0 10	101	31 7	15 8	47 7	4 8
15	27	408	12	0 10	24	32 8	12 4	48 9	5 9
9	27	528	8	0 10	12	34 2	10 7	47 8	7 3

[a] A E Bailey, R O Feuge, and B A Smith, *Oil & Soap*, **19**, 169–176 (1942)

hydrogenator will be much more efficient than can be obtained in commercial equipment In order to duplicate a laboratory prepared product in the plant, it will be necessary to adjust the factors of temperature, pressure, catalyst concentration, etc , in order to compensate for the unavoidable difference in agitation in the two cases

The effects of pressure and agitation on the fatty acid composition of hydrogenated oils are evident from the laboratory experiments on cottonseed oil which are detailed in Table 151 In these experiments the agitation was varied by simultaneously altering the speed of stirring and the size of the oil charge, the highest degree of agitation being obtained, of course, with the highest speed and the smallest charge It may be noted that increasing the agitation decreases the selectivity, and also inhibits iso oleic acid formation, and that increasing the pressure has the same effect as increasing the agitation

(e) Influence of the Catalyst

The nature of the catalyst has rather less influence upon the composition of the hydrogenated oils than might be expected Most of the catalysts used in commercial hydrogenation produce approximately equivalent products, even though they are prepared by such diverse processes as the decomposition of nickel formate by heat, the precipitation of nickel hydrate or carbonate with alkalies, with subsequent reduction of the dry powders, and the disintegration of an alloy of aluminum and nickel with caustic soda

Greater differences might be observed amongst products prepared with different catalysts if the latter consisted of metals other than nickel Richardson and Snoddy[20] found that platinum, for example, hydrogenated with much less selectivity than nickel, and with the formation of lesser quantities of iso oleic acid However, in present practice nickel is used for the hydrogenation of fats to the near or entire exclusion of other metals

Divergence from the normal behavior of nickel catalysts is chiefly to be found among catalysts which have been precipitated from nickel sulfate solution Such catalysts always contain at least traces of sulfates, probably in the form of basic nickel sulfate, although it is uncertain whether their peculiarity is due to this circumstance, or simply the fact that they are derived from a bivalent nickel salt At any rate, nickel sulfate catalysts produce characteristically high contents of iso oleic acid in the hydrogenated products[19] and yield a very hard fat The tendency of the hydrogenated oils to become hard at relatively high iodine values makes catalysts of this type generally unsuitable for the manufacture of high grade edible fat products The tendency of nickel sulfate catalysts to form much iso oleic acid is not necessarily accompanied by any unusual degree of selectivity, although in some cases such catalysts may apparently be almost incapable of hydrogenating oleic acid (see discussion of catalyst poisoning on page 583),

In considering the behavior of different nickel catalysts, it must be borne in mind that comparisons between two different catalysts on the basis of their total nickel content are valid only if the two are of equal activity Only a small proportion of the total metal in a catalyst is actually catalytically active, the remainder being altogether inert The important characteristic of a catalyst is not its total nickel content, but its content of active nickel The latter can be judged only on the basis of the activity of the catalyst The concentration of the catalyst is one of the important variables determining the composition of the hydrogenated oil, hence in comparing two different catalysts at equal concentrations of total nickel, one may have different products simply because one of the catalysts is more active than the other

[20] A S Richardson and A O Snoddy, *Ind Eng Chem*, **18**, 570–571 (1926)

The effect of varying the concentration of catalyst is apparent from the data in Table 152 Increasing the catalyst concentration has the effect of simultaneously making the hydrogenation more selective and causing more iso oleic acid to be formed

It may appear paradoxical that slowing the hydrogenation by reducing the pressure or agitation should make the reaction increasingly selective, whereas slowing it by reducing the catalyst concentration has a contrary effect All observed effects are entirely consistent, however, if the over all rate of conversion is disregarded, and the reaction is viewed from the more rational standpoint of the functioning of the catalyst Actually, the selectivity (or iso oleic acid formation) is related to the rate at which the catalyst operates, a rapid rate being conducive to low selectivity and low iso oleic acid formation The catalyst functioning rate is of course quite unrelated to the rate of hydrogenation, *per se*, since with a low concentration of catalyst each catalytically active particle may be functioning

TABLE 152

COMPARISON OF COTTONSEED OIL SAMPLES HYDROGENATED TO AN IODINE VALUE OF 62 9 WITH DIFFERENT CONCENTRATIONS OF THE SAME CATALYST, BUT WITH OTHER HYDROGENATION CONDITIONS CONSTANT (LABORATORY HYDROGENATIONS)[a]

Run No	Catalyst concentration % nickel	Hydrogenation time min	Percentage composition of fatty acids			
			Satd	Iso oleic	Oleic	Linoleic
16	0 025	98	35 1	11 0	45 7	8 2
12	0 050	31	34 1	11 2	47 5	7 2
15	0 100	24	32 8	12 4	48 9	5 9

[a] A E Bailey, R O Feuge, and B A Smith *Oil & Soap* **19**, 169-176 (1942)

rapidly, and yet there may be so little catalyst that the iodine value of the oil will fall relatively slowly Conversely hydrogenation may be rapid, yet if the concentration of catalyst is very high, there may be relatively long intervals between the moments when each active particle actually participates in the reaction

The relation of the rate of catalyst functioning to the composition of the hydrogenated oil is illustrated in Table 153 In this table all data from Tables 150, 151 and 152 have been collected, where these apply to hydrogenations with the same catalyst at a single temperature (300°F), and the catalyst functioning rate has been calculated in terms of iodine units reduced per minute per 1% of catalyst Allowance has been made for the inactivation of catalyst by poisons in the oil by arbitrarily assuming that 0 015% nickel is taken out of the reaction in this manner Thus upon the basis of this assumption, 0 100% nickel is corrected to 0 085%, 0 050% nickel is corrected to 0 035% and 0 025% is corrected to 0 010% This

correction seems reasonable on the basis of the behavior of the catalyst in this series of runs, and of past experience with similar catalysts and appears sufficiently accurate for the illustrative purposes of the table

It is evident from Table 153 that the hydrogenation time is not in itself a factor in determining the composition of the hydrogenated product

Although the tendency toward saturated or iso oleic acid formation is measured in ordinary batch hydrogenation by the rate at which the catalyst functions, there is some evidence that the actual factor determining these tendencies is the ratio of oil to hydrogen adsorbed on the catalyst If the relative proportions of adsorbed hydrogen and oil are variable under different hydrogenation conditions, it must be that increased pressure or agitation would enhance the transfer of hydrogen from the gas phase to the catalyst surface, and thus increase the adsorption of hydrogen relative to

TABLE 153
RELATION OF CATALYST FUNCTIONING RATE TO COMPOSITION OF COTTONSEED OIL HYDROGENATED TO 62 9 IODINE VALUE
(Laboratory hydrogenation at 300°F with a nickel catalyst)

Run No	Catalyst concn % nickel[a]	Hydrogenation time min	C F R[b]	Percentage composition of fatty acids			
				Satd	Iso-oleic	Oleic	Linoleic
23	0 285	190	0 7	31 0	20 4	44 6	4 0
11	0 085	101	4 4	31 7	15 8	47 7	4 8
19	0 035	67	15 9	32 8	13 2	48 1	5 9
15	0 085	24	18 3	32 8	12 4	48 9	5 9
12	0 035	31	34 4	34 1	11 2	47 5	7 2
9	0 085	12	36 5	34 2	10 7	47 8	7 3
16	0 010	98	38 1	35 1	11 0	45 7	8 2
17	0 035	21	50 8	35 2	10 2	46 2	8 4

[a] Corrected value 0 015% subtracted from actual value as allowance for catalyst poisoned by impurities in the oil
[b] Catalyst functioning rate, expressed in terms of iodine units reduction in oil per minute per 1% catalyst

that of oil, whereas increasing the catalyst concentration would offer a larger surface to compete for the available hydrogen, and thus have a contrary effect Upon the basis of this explanation, high selectivity and high iso oleic acid formation are favored by a low ratio of adsorbed hydrogen to adsorbed oil

Under most conditions of hydrogenation the velocity of the reaction is more or less proportional to the concentration of the catalyst It is possible, however, to use so much catalyst that the speed of hydrogenation will be governed entirely by the rate at which hydrogen can dissolve in the oil Under such conditions the time required to reduce the oil to a specific iodine value may not vary with considerable variation in the catalyst concentration

Hydrogenation catalysts are characterized by a strong affinity for the traces of soaps and other impurities which are found in all oils The

absorption of these has a "poisoning" effect on the catalyst, i e , the portions of the catalyst surface which combine with the impurities lose their ability to act catalytically The concentration to which the catalyst can be reduced in practice is limited by the necessity for providing a certain amount of active nickel for the absorption of poisons In the case of well-refined and bleached oils, the apparent amount of nickel poisoned by the oil is not generally greater than about 0 01%, calculated on the basis of the oil charge However, unrefined or unbleached oils, or soapy oils may inactivate a much greater amount of nickel Due to the tendency of the oil to slightly poison the catalyst, the speed of hydrogenation does not decrease regularly with decrease in the catalyst concentration as the latter falls to low values On the contrary, the hydrogenation rate decreases rapidly as the amount of catalyst approaches that required to absorb the poisons, and with any oil there is a catalyst level below which hydrogenation becomes impracticably slow With most oils and catalysts, this level is in the neighborhood of 0 02% to 0 03% where hydrogenation is to be practically complete, i e , where the iodine value of the oil is to be reduced to 10 to 20 units In the case of hydrogenation involving merely the substantial elimination of acids more unsaturated than oleic the poisoning effect of the oil is less marked, since a partially poisoned catalyst is inactivated with respect to its ability to convert oleic to stearic acid to a greater extent than with respect to its ability to convert less saturated acids to oleic acid

5 Catalysts for Hydrogenation

(a) *Theory of Catalyst Structure*

Since heterogeneous catalysis is a surface phenomenon, an essential requirement in an active catalyst is a highly extended surface With all other factors being equal, the smaller the individual catalyst particles, the more active the catalyst will be

In spite of the obvious relationship of surface area to catalyst activity, it does not follow by any means that the activity is determined solely by the magnitude of the surface area The latter may be made very large without the catalyst necessarily being very active In fact metallic nickel dispersed to the extent of being colloidal may be but an indifferent catalyst from the standpoint of activity All evidence indicates that the activity of a hydrogenation catalyst is due to a certain degree and kind of heterogeneity in the catalyst surface The development of this heterogeneity will not occur under all conditions but must be achieved by special methods of catalyst preparation

The various phenomena associated with heterogeneous catalysis are best explained on the basis of the "active spots' theory of Taylor [21] This theory

[21] H S Taylor, *Proc Roy Soc London*, A108, 105–111 (1925)

assumes that the metal atoms on the surface of the catalyst possess varying degrees of unsaturation, according to the extent to which they are elevated above the general catalyst surface, or otherwise released from the mutually restraining influence of their neighboring atoms. The relatively few metal atoms which are thus highly unsaturated are the ones which are capable of entering into temporary combination with the hydrogen and the unsaturated oil and in this way furthering the hydrogenation reaction. Each unsaturated atom or concentration of unsaturated atoms constitutes an

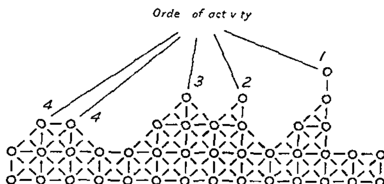


FIG. 75.—Schematic representation of a catalyst surface.

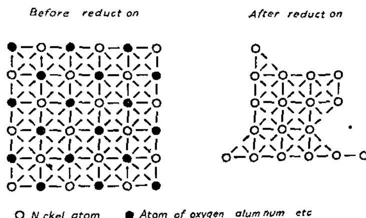


FIG. 76.—Schematic representation of the effect of reduction on a nickel catalyst.

active spot or center. The catalytic activity of each unsaturated atom corresponds to the extent of its unsaturation (Fig. 75).

Hydrogenation catalysts are seldom prepared directly from massive nickel but are made by first combining the nickel with other elements, as in nickel oxide, nickel hydrate, nickel carbonate, nickel formate, nickel aluminum alloy, etc., and then reducing the resulting compound to regain the nickel in metallic form. The efficacy of this procedure, in producing active nickel atoms relatively free from restraint by neighboring atoms, is evident from the schematic representation of catalyst reduction in Figure 76.

It is to be noted that according to the active spot theory, the most active nickel atoms, which are attached to the surface by a single constraining bond, are but one step removed from a gaseous state Armstrong and Hilditch[22] have considered it probable that such atoms are actually, momentarily detached from the catalyst, during the period of their catalytic functioning, and that the nickel thus actually operates in a gaseous form The subsequent migration and attachment of the nickel atom to the most exposed part of the catalyst surface is assumed to maintain a state of average similarity to the original catalyst

Since a strong adsorptive capacity for hydrogen is characteristic of hydrogenation catalysts, and since adsorption of hydrogen is presumably prerequisite to reaction of the hydrogen with the oil, numerous attempts have been made to correlate the phenomena of adsorption and catalytic activity However, *such attempts have not met with notable success* Although the two phenomena are doubtless to some extent related, there are discrepancies between catalytic activity and adsorptive capacity *per se*

The theories of Volmer[23] are of interest in connection with gas adsorption on the surface of hydrogenation catalysts According to the views of this writer, an adsorbed layer of gas molecules on the catalyst surface is able to flow freely over the surface in two dimensions Thus there is a flow of adsorbed hydrogen from regions of higher, to regions of lower concentration, with the latter corresponding to the active spots of Taylor

Catalysts are quite sensitive to heat, and may be rendered inactive by temperatures much below the fusion point of massive nickel Inactivation in this case is apparently the result of a sintering process, which causes the active, projecting nickel atoms to assume more stable positions on the catalyst surface Their sensitivity to heat makes their reduction to metallic form somewhat critical with respect to temperature, since there is usually not a large interval between the temperature at which reduction becomes rapid, and that at which sintering begins Catalysts precipitated in the form of nickel hydrates or carbonates on kieselguhr must usually be reduced within the range of about 800° to 1000°F

Freshly reduced catalysts which have not been in contact with oil are highly pyrophoric, due to the reactive nature of their unsaturated nickel atoms, and the fact that they retain much adsorbed hydrogen at the end of the reduction period If exposed to the air at this stage of their preparation and allowed to oxidize, they are completely inactivated Their pyrophoric properties and tendency to become inactivated through oxidation disappear, however, after the catalyst surface has become coated with oil This behavior of catalysts is of course readily explainable on the basis of the theory of active spots or unsaturated nickel atoms

[22] E F Armstrong and T P Hilditch, *Proc Roy Soc London*, **A108**, 111–120 (1925)
[23] N Volmer and P Mahnert, *Z physik Chem*, **115**, 239–252 (1925)

Hydrogenation catalysts of the precipitated type are almost invariably supported on diatomaceous earth, or other porous refractory material, and other catalysts, such as those prepared by the treatment of nickel alloys, are mixed with diatomaceous earth before use Supporting a catalyst in this manner so greatly increases its activity, and otherwise modifies its behavior, that there can be little doubt that the support contributes largely to the catalyst structure The support appears to protect the catalyst from sintering, since supported catalysts may be successfully reduced at somewhat higher temperatures than the corresponding unsupported catalysts It also appears reasonable to suppose that the presence of the support influences the dispersion of the catalyst particles and provides more numerous points for the attachment of unsaturated nickel atoms In addition, there is the possibility that silica, or other material in contact with nickel may tend to produce active nickel atoms, and hence that activity is centered at the boundaries between the nickel and the support The latter viewpoint is quite in accord with the common observation that the activity of a metallic catalyst may be enhanced or "promoted" by the presence of another metal or metallic oxide which is not in itself a catalyst for the reaction

(b) *Promotion of Nickel Catalysts*

A "promoter" is a metal or other substance which has the ability to enhance the activity of a catalyst, without being in itself a catalyst for the reaction in question The promotion of catalysts is much practiced in fields of catalysis other than the hydrogenation of fats, the employment of catalysts of two three, four, or even more components being by no means unusual In such complex systems the action of some of the components may more properly be described as synergistic rather than promotive, since usually more than one component will possess catalytic activity alone However, promotion in its proper sense is very common

A number of mechanisms have been proposed to explain the phenomenon of promotion It has been supposed that the promoter acts as a secondary catalyst, accelerating the formation or decomposition of intermediate compounds, that it assists in the adsorption of the reactants, or that it protects the catalyst from poisons However, in the case of catalysts for the hydrogenation of fats, it appears more reasonable to assume that the function of a promoter is simply structural, and that it permits the development of larger numbers of active centers on the catalyst surface

Promoters play a relatively minor role in the manufacture of fat hydrogenation catalysts since nickel catalysts of satisfactory activity can be pre
pared
prepar
noted, however, that hydrogenation catalysts are commonly supported on

a siliceous material, and that the latter may possibly serve as a promoter for the nickel

One of the useful promoters for precipitated nickel catalysts is aluminum oxide If a minor proportion of an aluminum salt is added to nickel nitrate solution before the latter is mixed with a solution of sodium carbonate, or other alkali, so that nickel and aluminum hydrates or carbonates are co precipitated, the resulting catalyst will usually be considerably more active after reduction than a product precipitated from nickel nitrate alone

The mixed carbonates of copper and nickel can be reduced at a tempera ture much lower than that required for the reduction of nickel carbonate alone, hence in the past there has been a considerable use of copper in hy drogenation catalysts simply for its effect on the reduction temperature[24] It has been suggested by Armstrong and Hilditch[25] that heat from the reduction of the copper produces local increases in temperature which are sufficient to permit reduction of nickel without the average temperature of the catalyst attaining a high value

(c) *Catalyst Poisoning*

Since the activity of a catalyst depends upon the presence of a relatively few metallic atoms of an unusually high degree of reactivity, it is to be ex pected that these atoms will display a marked avidity for many substances other than hydrogen or glycerides if such substances are present as im purities in the reacting system Furthermore if the impurities are of such a nature that they are not readily desorbed by the catalyst, but are held fast to the active atoms they will gradually concentrate on the catalyst surface, saturating the active atoms and rendering the catalyst inactive Substances which are thus able to cause catalysts to become inactive are termed catalyst "poisons" They may be troublesome when present even in traces in the reactants since the amount of catalyst is always small in relation to the amount of reactants and the active portion of the catalyst is in turn small in comparison with the total catalyst

Catalyst poisoning may be irreversible, leading to permanent inactivation of the catalyst, or it may be reversible, if under certain conditions the poison can be removed and the original activity of the catalyst restored Both reversible and irreversible catalyst poisoning are encountered in the hydrogenation of fats and oils

Among the more violent poisons for nickel catalysts are the gaseous sulfur compounds hydrogen sulfide carbon disulfide, sulfur dioxide, carbon oxysulfide, etc These compounds are of considerable concern in practical hydrogenation since they may occur as impurities in crude hydro

[24] J Dewar and A Liebmann, Brit Pat 12 982 (1913) U S Pats 1 268 692 and 1 275 405 (1918)

[25] E F Armstrong and T P Hilditch *Proc Roy Soc London* **A102** 27 32 (1922)

gen prepared by the steam iron or water gas–catalytic processes They are rapidly absorbed by nickel catalysts, and poison the catalysts irreversibly

Experience with the sulfur poisoning of commercial nickel catalysts is in general accord with the active spot theory of catalyst structure The amount of sulfur required to poison a catalyst is in direct proportion to the activity of the catalyst In the case of good catalysts, however, the amount of sulfur required for complete poisoning is rather larger than is to be expected from the assumption that the active nickel comprises a relatively small part of the total surface Although inactive catalysts may be poisoned by 0 5 to 1 0 gram sulfur per 100 grams nickel, active catalysts are not rendered substantially inoperative until they have absorbed 3 0–5 0 grams sulfur per 100 grams nickel If it is assumed that the sulfur is combined stoichiometrically with the nickel, to yield NiS, the above amounts of

TABLE 154

ACTIVITY VS SULFUR CONTENT OF A POISONED CATALYST

Approximate active nickel content of catalyst	6 5%
Experiment 1	
Calculated percentage of total nickel combined with sulfur (as NiS)	0 9
Residual active nickel %	5 6
Hydrogenation time required to reduce the iodine value of cottonseed oil from 107 to 25 min	30
Experiment 2	
Calculated percentage of total nickel combined with sulfur	2 9
Residual active nickel %	3 6
Hydrogenation time as above min	48
Experiment 3	
[illegible] of total n ckel combined with sulfur	6 0
	0 5
	280

sulfur *correspond to about* 5 5 9 0% of the total nickel in the catalyst

Experiments of the author with the three sulfur compounds, hydrogen sulfide carbon disulfide and sulfur dioxide have revealed that the amount of sulfur required to inactivate a given catalyst is substantially the same, regardless of the *compound from* which it is derived The avidity of catalysts for the sulfur in the three compounds varies somewhat, however, and increases in the order *that the compounds* are named

As stated above the amount of sulfur required to inactivate different catalysts varies directly with the catalyst *activity* When a single catalyst is progressively poisoned by the addition of successive portions of a sulfur containing compound, the activity *of the catalyst after* each addition corresponds closely to the residue of active nickel, as calculated from the sulfur added and the sulfur required for *complete poisoning* (Table 154)

Sulfur poisoning, it is to be noted, can result from sulfur compounds in the oil (although this is uncommon), from sulfur compounds in the hydrogen added to the oil, or from sulfur compounds in the hydrogen used to reduce the catalyst, if the latter is of the type that requires reduction with hydrogen Also, under certain conditions, sufficient sulfur to poison a catalyst can be derived from the catalyst itself

In the precipitation of catalysts from nickel sulfate solution, in the form of nickel hydroxide or nickel carbonate, there is invariably some nickel precipitated in the form of basic nickel sulfate The latter compound is relatively insoluble, and hence difficult to wash out of the finished catalyst During the reduction of catalysts containing basic nickel sulfate the greater part of the sulfates are reduced to sulfides which then appear to combine with the active or potentially active nickel in the catalyst The relationship between the sulfur content and the activity of catalysts of this type is shown in Table 155

TABLE 155
RELATIONSHIP BETWEEN SULFUR CONTENT AND ACTIVITY IN PRECIPITATED CATALYSTS FROM NICKEL SULFATE
(Activity of catalyst expressed in terms of minutes required to reduce cottonseed oil to an iodine value of 25 in successive runs)

Catalyst No	Sulfate S (unreduced catalyst)[a]	Sulfide S (reduced catalyst)[a]	Hydrogenation time min				
			Run 1	Run 2	Run 3	Run 4	Run 5
1	1.6	1.4	33	47	47	63	78
2	—	1.9	42	52	67	88	200
3	2.4	2.0	39	47	68	90	240
4	2.6	2.4	43	64	84	170	Failed
5	3.9	—	60	120	Failed	—	—
6	5.0	4.4	Failed	—	—	—	—

[a] Grams sulfur per 100 grams nickel

For sulfates to be capable of poisoning the catalyst, it is apparently necessary for them to be coprecipitated with the nickel, as sodium sulfate or other sulfates added to a catalyst *after* the latter is precipitated have no poisoning effect

Besides the sulfur compounds mentioned above, the catalyst poison most likely to cause trouble in the hydrogenation of fats and oils is carbon monoxide which is also present in small amounts in unpurified steam–iron and water gas–catalytic hydrogen Carbon monoxide is absorbed more slowly than are the sulfur compounds and poisons the catalyst reversibly It may be removed, and the catalyst restored to its original activity, by interrupting the hydrogenation and continuing to agitate the catalyst–oil mixture under a reasonably good vacuum (below about 25 in Hg) for a short time

The poisoning effect of carbon monoxide is highly dependent upon the

conditions, and particularly the temperature of hydrogenation If hydrogenation is conducted in the neighborhood of 400°F, carbon monoxide in the amount of 0 5% in the hydrogen will slow the operation to scarcely a noticeable degree At 350°F, its effect will be much more noticeable, and at 300°F it will not be possible to hydrogenate with hydrogen containing as little as 0 1% carbon monoxide, without frequent evacuation of the hydrogenator At a temperature of 200°F it is virtually impossible to hydrogenate oils with gas containing more than a few thousandths of one per cent of carbon monoxide The poisoning effect of carbon monoxide is relatively more troublesome at low hydrogen pressures (Fig 77)

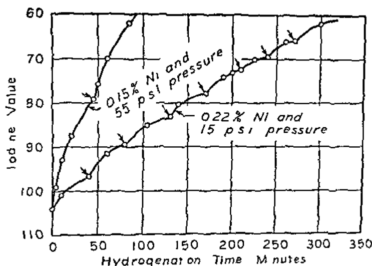


FIG 77 —Hydrogenation of cottonseed oil at a low temperature with hydrogen *containing traces of carbon monoxide Arrow indicates points at which hydrogenator* was evacuated to remove carbon monoxide

Typical hydrogenation curves of cottonseed oil hydrogenated at a low temperature with gas containing traces of carbon monoxide are shown in Figure 77

Most other gases which may be present as impurities in hydrogen, including carbon dioxide, nitrogen, and oxygen, are not catalyst poisons, although in a hydrogenation apparatus of the "dead-end" type they will of course slow the reaction if allowed to accumulate in the head space of the hydrogenator, and dilute the hydrogen therein Small amounts of water vapor in the hydrogen appear to have no poisoning effect

The matter of catalyst poisoning through impurities in the oil has been discussed to some extent previously, in connection with the effect of the catalyst concentration on the course of hydrogenation Not a great deal is known as to the natural oil and fat impurities which may function as catalyst poisons Free fatty acids in ordinary concentrations at least, have little or no effect on the activity of the catalyst The carotenoid

pigments likewise appear to be devoid of poisoning tendencies since there is no correlation between the color of an oil and the readiness with which it may be hydrogenated There are more or less definite catalyst poisons in most crude oils, however, for these oils are more easily hydrogenated after refining In most cases treatment of a crude oil with a liberal quantity of active bleaching clay is as effective in removing catalyst poisons as alkali refining

Sodium or other alkali soaps are very pronounced catalyst poisons Sufficient soap to seriously poison the catalyst will seldom be found in vegetable oils which have been well bleached after alkali refining, but lard edible tallow, or other light colored animal fats which require little or no bleaching are often soapy enough after refining to cause trouble in hydro genation Soap is quite effectively absorbed by used catalysts which have become largely inactivated, hence in hydrogenating alkali refined lard, etc the expedient is sometimes adopted of giving the fat a pretreatment with old catalyst before fresh catalyst is added

A wide variety of substances were tested for their effect on nickel catalysts by Ueno,[26] who reported the following to be poisons soaps of potassium, sodium, lithium, magnesium, barium, beryllium, iron, chromium, zinc, cadmium, lead, mercury, bismuth, tin, uranium, and gold, copper hydroxide, ammonium molybdate, boric, arsenious, and hydrochloric acids, glycollic, lactic, hydroxystearic, oxalic, succinic, fumaric, malic, citric, and tartaric acids, sodium taurocholate, iron, zinc, lead, mercury, sulfur, tellurium, selenium, and red phosphorous, proteins, blood albumin, blood fibrin, gelatin, glycerol, lecithin, sucrose, dextrose, mannitol, starch, morphine, strychnine, amygdalin, potassium cyanide, zinc oxide, and aluminum silicate The following were found to be without poisoning effect soaps of calcium, strontium, aluminum, cerium, nickel, manganese, copper, silver, vanadium, thorium, and platinum, nickel acetate, butyrate, stearate, lactate, oxalate, and succinate, tungstic acid, fatty acids, nucleic acid, nickel, tin, zirconium, aluminum, copper, hemoglobin, cholesterol, squalene, and glycogen

The effective life of a catalyst probably depends upon the extent to which it absorbs poisons from the oil Some slight content of poisonous substances appears to be unavoidable, even in the most carefully refined oils Even if the latter consisted of absolutely pure glycerides, it is quite possible that some degree of catalyst poisoning might occur, through the formation and adsorption of oxidation products or other degradation products of the oil

Partial poisoning of a catalyst may have an effect on other characteristics than its activity Sulfur-poisoned catalysts, for example, are inclined to be more selective than unpoisoned catalyst, since they hydrogenate linoleic

[26] S Ueno, *J Soc Chem Ind Japan*, **21**, 898–939 (1918)

acid to oleic acid quite readily, but are in some cases almost impotent with respect to the transformation of oleic acid to stearic acid However, these catalysts are inclined to produce large quantities of iso oleic acid Catalysts which have become partially inactivated through use produce hydrogenated fats slightly different from those produced by fresh catalysts, being inclined to form large amounts of saturated acids or to hydrogenate nonselectively, without being unusually efficient in the suppression of iso oleic acid formation

(d) Nickel Formate and Other Wet Reduced Catalysts

One method of preparing nickel catalysts which has long been popular comprises first converting the nickel to the easily decomposable salt of an organic acid, and then decomposing the salt by heat The latter operation, in which the nickel is reduced to the metallic form, is carried out while the catalyst is suspended in oil, hence catalysts of this type are termed "wet reduced" In the preparation of wet reduced catalysts, it is essential that the nickel salt be reducible at a low temperature below that at which thermal decomposition of the oil becomes pronounced Various nickel salts have been proposed for the purpose, but the one which has found by far the greatest amount of practical use is the formate, prepared by treating precipitated nickel hydroxide or nickel carbonate with formic acid

Nickel formate begins to decompose at about 300°F by the following reaction



$$Ni(OOCH)_2\ 2H_2O = Ni + 2CO_2 + H_2 + 2H_2O$$

Above about 375°F decomposition becomes rapid Theoretically, 100 pounds of nickel formate yield 31 8 pounds of metallic nickel

In practice, the reduction of nickel formate is carried out in specially designed closed vessels equipped for accurate temperature control The oil in which the catalyst is suspended may be of any type, although coconut oil, or other highly saturated oil is often preferred The ratio of oil to nickel formate in the charge is not critical, the use of 2 to 4 parts of oil to 1 of formate is common practice Ordinarily the rate of heating is as rapid as the design of the equipment permits The maximum temperature employed in reduction differs somewhat in different plants A temperature as high as 464°F is mentioned by one writer,[27] although reduction is often carried out at a substantially lower temperature Reduction is continued for an arbitrary time, which may be upwards of an hour, or until laboratory tests reveal that the product has attained the maximum activity During the reduction period, and also during the cooling period following reduction, a slow current of hydrogen is bubbled through the oil Since the reduction is thermal in nature, and involves no combination of hydrogen with

[27] O H Wurster, *Ind Eng Chem*, 32, 1193–1199 (1940)

oxygen in the catalyst, the chief function of the hydrogen is merely to sweep decomposition products out of the oil As the catalyst becomes active, hydrogenation of the oil begins, and at the end of the reduction period it is usually completely hardened

If the catalyst is to be used at once, the batch is cooled to about 200°F, kieselguhr equivalent to about four times the weight of the nickel is added, and the hardened oil is filtered off from the catalyst and fresh oil substituted The fresh oil is, of course, of the same kind as that which is to be hydrogenated In some cases the mixture of catalyst and hardened oil may be added directly to the hydrogenator without the substitution of fresh oil, but in the manufacture of edible products this procedure is seldom followed, inasmuch as the hardened oil will be somewhat high in free fatty acid content, and will have suffered some degree of thermal decomposition If the catalyst is to be stored or shipped the mixture of catalyst and hardened oil is often cast into blocks or formed into flakes over a chill roll

Nickel formate catalysts have good activity and desirable characteristics with respect to selectivity and the formation of iso oleic acids They can be made somewhat more uniform than can dry reduced catalysts prepared by most methods Since the catalyst is activated while in contact with oil, the somewhat troublesome operation of transferring the reduced catalyst to oil without access to air is avoided

The chief disadvantage of wet reduced catalysts is that they are inclined to contain nickel particles of colloidal or near colloidal dimensions, which are very difficult to filter from the oil after hydrogenation is completed The formation of colloidal nickel may be minimized by careful attention to the reduction temperature and time, but even under the best conditions, wet reduced catalysts are relatively difficult to filter cleanly from the oil Oils hydrogenated with wet reduced catalysts must usually be treated with bleaching earth or otherwise refined to insure complete removal of the catalyst whereas good dry reduced catalysts can in most cases be removed completely by simple filtration

If nickel carbonate is precipitated together with copper carbonates, the resulting mixture can be reduced at a temperature sufficiently low (170–180°C) for wet reduction to be feasible [24] There has, in the past been a considerable use of wet reduced nickel–copper catalysts

(e) *Dry Reduced Catalysts*

Dry reduced catalysts are prepared by precipitating nickel hydroxide or nickel carbonate on diatomaceous earth or other refractory support, drying and grinding the precipitate, and reducing the resultant powder at a high temperature with a current of hydrogen The preparation of dry reduced catalysts differs fundamentally from that of wet reduced catalysts in that the activity of the former is determined primarily in the step of precipita

tion, whereas the activity of the latter depends principally upon the conditions of reduction. Dry reduced catalysts are of course finally activated by reduction, but this latter operation is relatively simple and straightforward, as compared with the highly critical process of precipitation.

Since nickel sulfate is the cheapest and most readily available nickel salt, it often serves as the starting material for dry reduced catalysts. However, nickel catalysts precipitated directly from the sulfate have the property of producing excessive amounts of iso oleic acids, hence for most purposes nickel nitrate is a preferable material. Nickel nitrate may be prepared directly by the action of nitric acid on the metal, or by precipitating nickel sulfate solution with an alkali and dissolving the precipitate in nitric acid.

Alkalies used for precipitating the catalyst include sodium hydroxide, ammonia, sodium carbonate, and sodium bicarbonate, with the last mentioned being perhaps the most generally suitable. Diatomaceous earth equivalent to 1 to 2 times the weight of nickel is suspended in the solution of nickel salt at the beginning of the precipitation, to provide a support for the catalyst.

The activity of a catalyst of this type is dependent to an overwhelming degree upon such operating details as the temperature at which precipitation takes place, the rate at which the nickel salt and alkali solutions are mixed, the excess of alkali employed, the boiling to which the suspended precipitate is subjected, etc. Suitable conditions for the preparation of an active catalyst must be established by trial and error, and once they are established it will be found that even minor deviations may affect the activity of the catalyst very greatly. In fact, even the most careful standardization of the manufacturing procedure will scarcely suffice to eliminate all variations in the catalyst, in the author's experience at least, it is quite impossible to prepare catalysts of uniform activity by ordinary methods of precipitation. The electrolytic method of precipitation, to be described later, is recommended for the production of the most uniform and active catalysts.

The following are two methods of precipitation which have been found to yield active catalysts from nickel sulfate and nickel nitrate, respectively.

Method No. 1. 240 pounds of $NiSO_4 \cdot 6H_2O$ are dissolved in 1100 gallons of distilled water and the solution is brought to boiling. To the solution is added 60 pounds of kieselguhr. A fresh solution of 145 pounds of $NaHCO_3$ in 300 gallons of cold distilled water is made up separately, and this is added uniformly over a period of 1.0–1.5 hours to the $NiSO_4$ solution while the latter is kept continuously and vigorously boiling. There are then added 60 pounds of additional kieselguhr and the boiling is continued for 0.5 to 1.0 hour longer. At the end of this time the solution should be slightly alkaline to phenolphthalein. The precipitated catalyst is filtered out, resuspended in 1000 gallons of distilled water, boiled for a short time and refiltered. This last operation is repeated once or twice more, and the catalyst

is then filtered, dried and ground It should dry to the form of a friable cake, easily disintegrated in the fingers to a fine powder of high specific volume This catalyst requires about 8 hours reduction at 900–950°F, and contains about 24% nickel in the unreduced form

Method No 2 $Ni(NO_3)_2$ equivalent to 27 pounds of nickel is dissolved in 500 gallons of distilled water, and 25 pounds of kieselguhr are added Fifty pounds of 16 Bé sodium hydroxide and 20 pounds of aluminum powder are mixed, and after foaming has subsided, 60 pounds of sodium bicarbonate are added and the solution is made up to 300 gallons with distilled water The latter solution is then added to the $Ni(NO_3)_2$ solution over a period of 1 hour, while the temperature of the latter is raised from about 150°F to boiling It is unnecessary for the aluminum to become completely dissolved during this operation After precipitation is complete, the precipitated catalyst is filtered resuspended in water, again filtered and resuspended, filtered, dried and ground This catalyst contains about 22% nickel before it is reduced and requires a temperature of about 1000°F for reduction

There is on the market a special "hydrogenator's fluffy nickel carbonate," where merely requires to be boiled in water with an equal weight of kieselguhr to produce a fairly active and uniform catalyst

The apparatus commonly used for the dry reduction of catalysts consists of a horizontal steel drum with conical ends, which may be slowly revolved upon its longitudinal axis The drum is placed inside an insulated housing equipped with gas burners, which serves as a furnace Hydrogen inlet and outlet pipes are provided to permit a current of hydrogen to be passed over the surface of the catalyst in the drum After reduction is complete, which is usually a matter of several hours, the apparatus is cooled, the hydrogen flow is shut off, and the hydrogen inside the drum is displaced with a current of carbon dioxide A tailpipe of large diameter attached to one of the conical ends of the drum is then uncapped, and the drum is tilted so that the reduced catalyst will discharge by gravity below the surface of oil contained in a small tank or drum The discharge of reduced catalyst must be slow, and accompanied by intensive stirring of the oil, to prevent unwetted catalyst from floating to the surface of the oil and becoming oxidized and inactivated upon contact with the air The slurry of oil and catalyst resulting from the above series of operations will usually contain 8% to 10% of nickel, and may of course be added directly to charges of the same oil in the hydrogenators

A furnace for accomplishing the dry reduction of catalysts continuously has been described by Sieck [28]

(f) Electrolytically Precipitated Nickel Catalyst

A recently introduced method of catalyst preparation, which yields a product of very high activity, good characteristics, and remarkable uniformity, is that of electrolytic precipitation This method involves the corrosion of sheets of metallic nickel in an electrolyte by the passage of a

[28] H Sieck, *Oil & Soap*, **16**, 24–25 (1939)

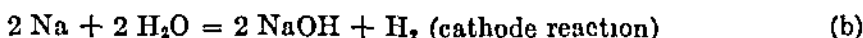
direct current The nickel is precipitated in the form of nickel hydrate, on kieselguhr suspended in the electrolyte

The superiority of the electrolytic method over other methods of precipitation appears to be due to the fact that by this means the entire mass of catalyst can be precipitated at a constant and controllable *p*H, whereas in ordinary precipitation by the addition of one solution to another, the *p*H of the precipitant solution continuously varies The electrolytic process, as first introduced by the American firm of Sieck & Drucker, employed an electrolyte of ammonium chloride and sodium acetate, and relied upon buffering of the electrolyte to maintain the *p*H of the latter within reasonable limits However, later experience revealed that it was more satisfactory to control the *p*H in a more positive manner, by the constant addition of a suitable acidic substance during the course of reaction With the *p*H thus controlled, ordinary 1% sodium chloride solution, made from salt of A C P grade, was found to be a satisfactory electrolyte

The reactions occurring in the cell are as follows



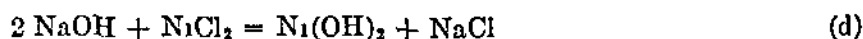
$$2\,NaCl = 2\,Na + 2\,Cl \qquad (a)$$



$$2\,Na + 2\,H_2O = 2\,NaOH + H_2 \text{ (cathode reaction)} \qquad (b)$$



$$2\,Cl + Ni = NiCl_2 \text{ (anode reaction)} \qquad (c)$$



$$2\,NaOH + NiCl_2 = Ni(OH)_2 + NaCl \qquad (d)$$

With respect to the electrolyte, the process is theoretically self regenerative, as no sodium chloride is used up in the reaction In practice, however, there is always formation of basic nickel chloride to some slight degree This abstracts chloride ions from the solution, leaving an excess of sodium ions and causes the electrolyte to gradually become alkaline The tendency of the electrolyte to become alkaline must be counteracted by the constant addition of some acid Gaseous carbon dioxide has been found to be a convenient acidic substance for control of the *p*H, being simply bubbled from a cylinder into the bottom of the cell at the proper rate during the course of operation

A sheet of electrolytic nickel is used as the anode, and sheets or screens of the same size, made of nickel or other nonrusting metal serve as the cathodes Low voltage, high amperage direct current is passed through the cell at a rate sufficient to maintain a current density of approximately 55 amperes per square foot on either side of the corroded nickel sheet The electrolyte, contained in a wooden, ceramic, or *nonrusting alloy tank, is* heated to 120–125°F during the operation, and is stirred, to maintain in suspension kieselguhr equivalent to the weight of nickel to be corroded The *p*H of the electrolyte is highly important, and must be maintained between 9 0 and 9 5

At the end of the precipitation period the catalyst is filtered out, washed

free of sodium chloride with distilled water, dried, ground, and dry-reduced at about 900°F for about 4 hours

(g) *Nickel Alloy Catalysts*

A novel catalyst devised by Raney[29] has been used quite extensively, not only for the hydrogenation of fats and oils, but also for various other commercial hydrogenation processes

In the manufacture of Raney catalyst, nickel is first alloyed with aluminum, the most common proportions of the two metals being about 1 1 by weight The alloy, upon cooling, is friable and easily reduced to a fairly fine powder The catalyst is marketed in the form of such a powder

The catalyst is prepared for use by the following procedure In an open digestion tank is placed a considerable excess of strong (about 20%) sodium hydroxide solution To this solution the desired amount of powdered alloy is slowly added, the rate of addition being limited by the tendency of the solution to foam out of the tank Much heat is generated by the reaction between sodium hydroxide and aluminum, so that heating of the solution is unnecessary during the addition of the powder Proper disposition must of course be made of the hydrogen liberated during the reaction After the alkali solution and powder have been combined, the contents of the tank are heated to 245–250°F, and held at this temperature for 2 to 3 hours At the end of this time the catalyst will be in the form of a sludge consisting almost entirely of metallic nickel, the aluminum being in solution in the form of sodium aluminate The sodium aluminate and excess alkali are then removed by repeated washing with cold water, followed in each case by decantation of the wash water from the settled catalyst sludge The washing must be very thorough, as even traces of alkali left in the catalyst will form a sufficient quantity of soap to effectively poison it when it is placed in contact with oil

After washing is completed, the last wash water is drawn off as cleanly as possible, and the residual sludge is covered with oil Heat is then applied, and vacuum, if it is available, to dry the sludge, and replace the protective water with oil The catalyst is highly pyrophoric, hence it would become inactivated if dried without protection from the air The finished catalyst is in the form of relatively large particles, and normally it occasions little trouble in filtration However, kieselguhr is usually added to the oil–nickel sludge after the latter is dried Drying of the catalyst is preferably carried out in a separate tank from that used for digestion, otherwise it is very troublesome to remove all traces of the added oil before the next batch of catalyst is digested Any trace of oil in the digestion tank is inclined to form soaps which are highly poisonous to the catalyst

[29] M Raney, U S Pats 1 563 587 (1925), 1,628,190 (1927), and 1,915 473 (1933), *Ind Eng Chem*, 32, 1199–1203 (1940)

Raney nickel produces hydrogenated oils similar to those made with good wet- or dry reduced catalysts under comparable conditions of hydrogenation It is somewhat deficient in activity as compared with the best reduced catalysts, but is popular with many hydrogenators because of the simplicity of the method by which it is activated It avoids the use of complicated reducing furnaces, etc , and even does not require distilled water in its preparation

(h) *Metals Other Than Nickel as Catalysts*

There is at the present time probably little, if any, use of metals other than nickel for ordinary hydrogenation of fats and oils Both platinum and palladium are effective hydrogenation catalysts, and are operative at temperatures considerably below those at which it is possible to use a nickel catalyst However, they are less selective than nickel, and as pointed out by Richardson and Snoddy,[20] would probably be generally inferior to nickel even if their high cost did not preclude their use

Mixed non nickel catalysts of the metal–metal oxide type, as for example, copper–chromium oxide, are recommended by Paterson[30] for hydrogenation of fats in conjunction with nickel catalysts, because of their strong decolorizing action These catalysts are operative only at relatively high temperatures and pressure, and are normally used for the reduction of carbon to oxygen rather than carbon to carbon double bonds However, it is claimed that the reduction of carbon oxygen linkages in the glycerides can be made negligible by proper attention to the temperature, pressure, reaction time, etc

Catalysts for hydrogenations of fatty materials other than the ordinary reduction of carbon carbon double bonds will be considered in a later section under the heading of the individual hydrogenation products

6 Hydrogen Production and Purification

(a) *The Electrolytic Process*

The purest hydrogen, containing only negligible amounts of other gases, is produced by the electrolysis of dilute water solutions of acids or alkalies In most modern installations the electrolyte used is sodium hydroxide The electrolytic method is in many respects the simplest method of making hydrogen, and in addition it produces a gas which is perfectly free of catalyst poisons It is equally efficient in large and small installations It is relatively expensive, however, both with respect to the initial cost of the plant and the cost of operation, and hence is no longer widely used except in regions where there is an abundance of cheap hydroelectric power and a scarcity of coal

[30] W J Paterson (to Lever Bros Co), U S Pat 2 307 065 (1943)

The essential parts of an electrolytic hydrogen plant are a motor-generator combination, or other source of direct current, a number of electrolytic cells for the actual generation of hydrogen, a hydrogen holder for receiving hydrogen from the cells, a hydrogen compressor, and high pressure storage tanks for receiving the compressed gas Normally, oxygen is a by-product of the process, and equipment must also be provided for receiving, compressing, and bottling the oxygen

Each cell consists essentially of a tank to hold the electrolyte, usually of narrow width and rectangular in form, a metal cathode and anode, and a diaphragm of asbestos to separate the cathode and anode The diaphragm is designed to prevent intermingling of the evolved hydrogen and oxygen and yet not be impermeable to the electrolyte The cells are usually built in a standard size, with a capacity of the order of 10 cubic feet per hour each, any desired capacity in the plant being attained by employing the proper number of cells

The design, and to some extent the operation of an electrolytic hydrogen plant generally involve a compromise between fixed charges determined by the investment in the plant, and operating charges for electric current Considerable latitude is allowable in the operating conditions, the capacity of a plant of given size and cost may be increased by increasing the amperage applied to each cell If the capacity is increased in this manner, however, there is at the same time a decrease in the efficiency of the plant, in terms of cubic feet of hydrogen produced per kilowatt-hour of current consumed

Modern developments in the design of electrolytic hydrogen cells have been in the direction of attempts concurrently to improve the capacity and efficiency of the cells Since the passage of a definite quantity of current will always produce the same amount of hydrogen, regardless of the type of cell, the efficiency of the latter is to be measured in terms of the voltage required for its operation Current amounting to 1 ampere hour liberates 0 01482 cubic foot of hydrogen measured at standard temperature and pressure, or about 0 016 cubic foot measured at ordinary temperature Therefore, the cubic feet of hydrogen produced per kilowatt hour of current is equivalent to 16 divided by the voltage In the more efficient cells, the voltage required is about 2 volts, so that the production per kilowatt hour is about 8 cubic feet Or stated in another way, about 125 kilowatt hours of current are required for each 1000 cubic feet of hydrogen produced

According to figures furnished by Taylor,[31] substantially greater economy in the way of current consumption is hardly to be expected, regardless of possible future improvements in cell design The theoretical decomposition potential of water, in the absence of overvoltage, is 1 23 volts, and with any form of technically feasible electrodes, the overvoltage increases this po-

[31] H. S Taylor, *Industrial Hydrogen* Chemical Catalog Co , New York, 1921

tential to not less than 1 5 volts The necessity of providing a further potential to overcome the resistance of electrolyte and diaphragms further increases the minimum practical voltage to very nearly 2 volts

(b) *Steam–Iron Process*

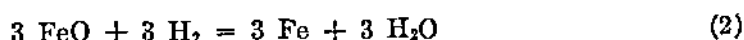
Most of the hydrogen produced for fat hardening in the United States is made by the steam–iron process This process is cheaper than the electrolytic process, both with respect to the initial cost of the plant and the cost of subsequent operation Steam–iron plants are economical in capacities of about 2500 cubic feet per hour upwards In the past the chief deterrent to their use has been the relative impurity of the hydrogen produced Efficient purification processes are now available for steam–iron hydrogen, however, and the best operated plants produced hydrogen which compares very favorably in purity with electrolytic hydrogen

In principle the steam iron process is simple, involving merely the alternate oxidation and reduction of a hot iron ore mass Reduction is accomplished by means of the hydrogen and carbon monoxide in ordinary blue gas, made by blowing hot coke with steam In the oxidation cycle the ore mass is blown with superheated steam, with the oxygen of the latter combining with the previously reduced ore, and the hydrogen being set free The exact changes in the oxygen content of the iron mass in practical operation have not been fully established, but are commonly supposed to be as follows

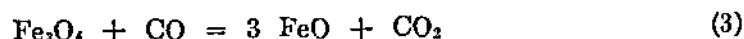
Reduction



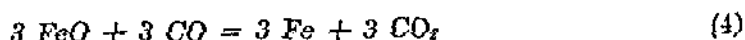
$$Fe_3O_4 + H_2 = 3\ FeO + H_2O \quad (1)$$



$$3\ FeO + 3\ H_2 = 3\ Fe + 3\ H_2O \quad (2)$$

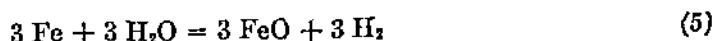


$$Fe_3O_4 + CO = 3\ FeO + CO_2 \quad (3)$$

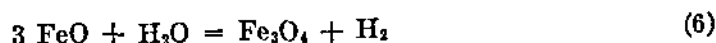


$$3\ FeO + 3\ CO = 3\ Fe + 3\ CO_2 \quad (4)$$

Steaming

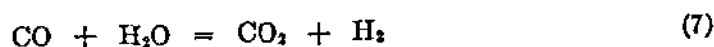


$$3\ Fe + 3\ H_2O = 3\ FeO + 3\ H_2 \quad (5)$$



$$3\ FeO + H_2O = Fe_3O_4 + H_2 \quad (6)$$

Also there is some tendency for the interaction of carbon monoxide and steam during the reduction cycle to produce carbon dioxide and hydrogen



$$CO + H_2O = CO_2 + H_2 \quad (7)$$

Thus carbon monoxide may either function directly as a reducing agent, or indirectly, through the production of hydrogen by the above reaction

In addition to the above reactions, there are side reactions which do not contribute to hydrogen production, but may be mentioned because of

their effect on the purity of the hydrogen. At the high temperatures prevailing in the steam–iron generator, reduced iron catalyzes the reaction



$$2\ CO = CO_2 + C \qquad (8)$$

It is due to this reaction that there is always a slight deposit of carbon on the ore mass at the end of the reduction period. During the subsequent period of steaming any carbon thus deposited reacts with the steam to produce both carbon dioxide and carbon monoxide as impurities in the hydrogen.



$$C + H_2O = CO + H_2 \qquad (9)$$



$$C + 2\ H_2O = CO_2 + 2\ H_2 \qquad (10)$$

Blue gas ordinarily contains in the neighborhood of 0.2% of hydrogen sulfide or other gaseous sulfur compounds. During the reducing phase these tend to combine with the iron contact mass, to form iron sulfide. The iron sulfide is in turn reactive with steam, so that a considerable part of the sulfur in the blue gas eventually finds its way into the hydrogen, in the form of hydrogen sulfide and traces of organic sulfur compounds.

In practice it will be found that carbon and sulfur will be deposited on the contact mass more rapidly than they are removed. Hence it is customary to follow each steaming period with a short period of aeration, during which air is blown through the ore to burn off carbon and sulfur accumulations. Failure to remove these accumulations is said to result in virtually complete inactivation of the contact mass.[32]

An additional source of impurities in steam–iron hydrogen is the reducing gas itself. After each reducing period, the generator is purged with steam for a few seconds before collection of hydrogen is begun, but this is insufficient to quite eliminate all blue gas from the system. Prolonged purging is of course wasteful of hydrogen.

The composition of unpurified steam–iron hydrogen varies somewhat according to the type of generator and its mode of operation, but will ordinarily be approximately as follows:

Carbon dioxide	0.5–1.0%
Carbon monoxide	0.2–0.5%
Oxygen	0.0–0.1%
Nitrogen	0.3–1.0%
Hydrogen sulfide	0.05–0.15%
Organic sulfur	0.1–0.5 grain per 100 cubic feet
Hydrogen	98.0–99.0%

In the United States the hydrogen generator in most common use is of the Bosch or Bamag type. This generator, which is illustrated in Figure

[32] S. Hurst, *Oil & Soap*, **16**, 29–35 (1939).

78, consists of a single tall cylinder, lined with firebrick and insulating brick The space within the generator is divided into two superimposed sections In the lower section is a grate supporting the iron ore contact mass, the upper section is filled with a checkerwork of firebrick, which serves as a steam superheater Connections are provided at the extreme top of the generator for air and steam, and between the contact mass and the superheater for air In a large line leading from the bottom of the generator is a cross, with quick-opening valves from the latter leading to a blue gas inlet line, a hydrogen outlet line, and a purge line All valves, in

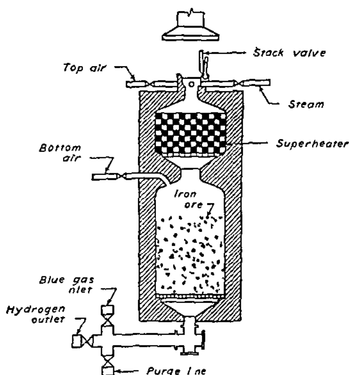


Fig 78—Hydrogen generator, Bamag type

cluding those mentioned above, and the stack valve, are interlocked and operated from an elevated platform near the top of the generator

The generator is operated at a temperature in the neighborhood of 1500°F, and as continuously as is feasible, since considerable time is required to warm up a cold unit The complete operating cycle comprises the following successive operations

Reducing—Blue gas is drawn from the blue gas holder and delivered to the bottom of the generator by a centrifugal blower, designed to produce a pressure of 20 to 30 inches of water It passes up through the hot contact mass reducing the latter, and at the bottom of the superheater meets a current of bottom air Combustion of the partially spent blue gas with this air in the superheater stores up heat in the latter for the subsequent steaming period

Purging—The blue gas is shut off, and hydrogen production is begun by passing steam through the superheater and then down through the contact mass The first portions of gas are discharged through the purge line to the atmosphere, to sweep out of the system the blue gas remaining there at the end of the reducing period

Steaming—The purge valve is closed, the hydrogen outlet valve is simultaneously opened, and steaming is continued The hydrogen produced is collected

Air blowing—Top air is blown through the generator from top to bottom, to burn off accumulations of carbon and sulfur on the contact mass

Reducing—Blue gas is again delivered to the generator, etc

The times allowed for the different portions of the cycle are governed by considerations of economy There is, of course, a steady diminution in the rate of hydrogen production as steaming is continued, and a similar diminution in the rate of iron oxide reduction during the reducing period The amount of hydrogen produced during the average period of steaming is governed by the amount of reduction accomplished in the corresponding reduction period The reduction and steaming periods are, therefore, approximately equal in length, and may be in the neighborhood of 10–15 minutes Both the purging and burning-off periods are much shorter

Steam-iron plants are operated to obtain the greatest economy consistent with good productive capacity and satisfactory purity in the hydrogen The factors governing economy, capacity, and purity are so involved that any detailed consideration of them is much beyond the scope of this book However, a few general principles may be briefly mentioned

The largest single item of expense in making steam-iron hydrogen is coke for the manufacture of blue gas Blue gas manufacture is a fairly well standardized process, and the coke requirements of different plants, in terms of the volume of blue gas produced, do not vary greatly There are large differences, however, in the efficiency of hydrogen generators, depending upon their design and mode of operation In general, practice in steam-iron hydrogen generation has improved greatly within the past 10 to 20 years Formerly, a consumption of blue gas amounting to 2 5–3 0 times the volume of hydrogen produced was considered good practice In the best modern plants blue gas-hydrogen ratios as low as 1 7 to 1, or even 1 5 to 1 are obtained The latter ratio corresponds to a coke consumption of about 45 to 50 pounds per 1000 cubic feet of hydrogen

Since the reactions represented by equations (1) to (8) are all reversible, with an equilibrium point depending upon the temperature of reaction as well as the concentration of reactants it is obvious that all of the factors mentioned above will be affected by the temperature at which the generator is operated, the composition of the blue gas, and the reducing-steaming cycle adopted A detailed discussion of the equilibria involved in the manufacture of steam-iron hydrogen is furnished by Taylor,[31] who particularly points out the importance of working principally on the Fe_3O_4–FeO cycle (Equations 1, 3, and 6) rather than the FeO–Fe cycle (Equations

2, 4, and 5), and at a relatively high temperature, in order to obtain maximum economy in the consumption of blue gas Actually, the reactions occurring in a steam–iron hydrogen generator are undoubtedly more complex than as represented by Taylor or the preceding equations, owing to the tendency of metallic iron and the various iron oxides to form a continuous series of solid solutions[33] comprising materials containing both less oxygen than FeO and more oxygen than Fe_3O_4 In practice the utilization of both steam and blue gas is more efficient than can be predicted from Taylor's data

While the over all reaction is theoretically exothermic, radiation losses from the generator and the necessity for heating excess quantities of steam and reducing gas require that a certain proportion of blue gas be burned to maintain the temperature of the generator Radiation loses are greatly reduced in single unit generators, however, and particularly those of large size, in comparison with the older multiretort units

The type of iron ore employed has an important bearing on the efficiency of steam–iron generators Ore from only a few localities has the requisite properties of high reactivity and sufficient ruggedness to withstand prolonged use without disintegration

The purity of steam–iron hydrogen is much less a problem now than formerly, since methods are available for efficiently removing all of the impurities mentioned previously, with the exception of the nitrogen In the better operated plants, hydrogen is now quite commonly produced with a purity in excess of 99 5% with the impurities consisting of nitrogen and methane, both of which are inert toward hydrogenation catalysts The individual purification processes will each be discussed in a later section

A frequent cause of impure hydrogen is contamination with blue gas due to a leaking valve in the blue gas inlet or hydrogen outlet lines (Fig 78) In the Bamag generator the pressure in the blue gas line is greater than that in the hydrogen line, consequently a leak in either valve will permit blue gas to flow back into the hydrogen These valves are of large size, and of necessity of the quick opening type, and are rather difficult to keep absolutely tight An expedient which has been very successful in eliminating gas leakage is the installation of small, low pressure steam lines leading to the space between the two halves of the gates in these valves With steam pressure in excess of the hydrogen or blue gas pressure turned into this space each time that the valves are closed, gas leakage is effectively prevented

In addition to Bamag generators, there are in the United States a number of installations of the Lane or multiretort type In this, the first type of steam–iron generator developed, the iron ore is contained in a number of small generators rather than one large one, and heat is supplied by burning

[33] E D Eastman, *J Am Chem Soc*, 44, 975–998 (1922)

blue gas on the outside of the retorts rather than within The blue gas supplied with the Lane system, unlike that used with single retort generators, is customarily purified to remove hydrogen sulfide Raw hydrogen from Lane plants is purer than that produced in single retort generators, but the former require more blue gas per unit volume of hydrogen produced, and are generally considered more expensive to operate

In Europe the Messerschmitt generator has been popular Like the Bamag generator, it consists of a single retort but the steam superheater is centrally located, and the ore is contained in an annular space between the superheater and the shell For additional information relative to the design of the various types of generators, the reader is referred to the publications of Taylor,[31] Hefter Schonfeld [34] Hurst,[32] etc

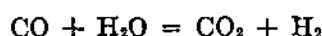
Bamag generators are most commonly built in units with nominal capacities of 2500, 5000, or 10,000 cubic feet per hour

In addition to the hydrogen generator proper, equipment required for a complete steam–iron plant includes a blue gas generator, gas holders for both blue gas and hydrogen, a water scrubber and cooler for the crude hydrogen obtained from the generator, air and blue gas blowers, a hydrogen compressor, high pressure hydrogen storage tanks, and equipment for purifying the hydrogen

Efficient operation of a steam–iron hydrogen plant requires metering and accounting of steam, coke, blue gas, and hydrogen, frequent analysis of both blue gas and hydrogen, and constant and expert attention to all operating details Checking of the hydrogen purity is much facilitated by the ready adaptability of continuous indicators or recorders of the thermal conductivity type

(c) *The Water Gas–Catalytic Process*

A third process for the manufacture of hydrogen for fat hardening is the water gas–catalytic process This process depends upon the so called water gas shift reaction,



$$CO + H_2O = CO_2 + H_2$$

which is catalyzed by various metallic or metallic oxide catalysts

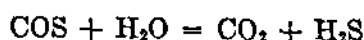
As a first step in this process, blue gas is made in the usual way, by the action of steam on coke, but with a maximum content of carbon monoxide and hydrogen, and a minimum content of nitrogen The blue gas is then compressed mixed with an excess of steam, and the mixture is superheated by passage through coils in a gas or oil fired furnace The superheated mixture is passed through a bed of catalyst in a separate reaction chamber, where the actual conversion indicated above occurs A temperature of

[34] G Hefter and H Schonfeld, *Chemie und Technologie der Fette und Fettprodukte* Vol II, Springer, Vienna, 1939

about 750°F is maintained in the reaction chamber A gas to gas heat exchanger is inserted in the inlet and outlet lines to the superheater-reaction chamber combination to transfer heat from the exit to the inlet gases In addition to the reaction above, the following reaction occurs between the steam and organic sulfur compounds in the gas, for example



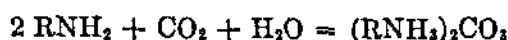
$$CS_2 + 2\,H_2O = CO_2 + 2\,H_2S \quad \text{and}$$



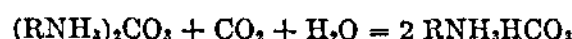
$$COS + H_2O = CO_2 + H_2S$$

so that any sulfur compounds in the treated gas are in the form of hydrogen sulfide

From the reaction chamber the gas is led to a cooler, and thence to countercurrent absorbers consisting of packed or tray and bubble cap towers, where the carbon dioxide and hydrogen sulfide are scrubbed out by mono ethanolamine or other amines The reactions between the amines and these gases are as follows



$$2\,RNH_2 + CO_2 + H_2O = (RNH_3)_2CO_3$$



$$(RNH_3)_2CO_3 + CO_2 + H_2O = 2\,RNH_3HCO_3$$



$$2\,RNH_2 + H_2S = (RNH_3)_2S$$



$$(RNH_3)_2S + H_2S = 2\,RNH_3HS$$

Each of the above reactions is reversible at moderately elevated temperatures, i e, slightly above the boiling point of water, consequently, the amines may be regenerated by heat[35] In this respect they present a marked advantage over caustic soda or other inorganic alkalies, which require chemical treatment for recausticization or regeneration Regeneration of the saturated amine is accomplished by passing it through a heat exchanger and then down a stripping column counter to a current of stripping steam generated in a reboiler in the base of the column

The hydrogen issuing from the amine absorber towers following the first stage of carbon monoxide conversion has approximately the following impurities

Carbon monoxide	1 5%
Carbon dioxide	Less than 0 2%
Oxygen	Less than 0 05%
Nitrogen	1 0–1 5%
Hydrocarbons	0 3%
Organic sulfur compounds	0 0–0 1 grain sulfur per 100 cubic feet

Gas of the above composition is even higher in carbon monoxide than crude steam–iron hydrogen, and like the latter, must be further purified before it is suitable for use in low temperature hydrogenation

The power and material requirements of the water gas–catalytic process

[35] L B Gregory and W G Scharmann, *Ind Eng Chem*, 29, 514–519 (1937) W R Wood and B D Storrs, *Proc Am Petroleum Inst III*, 19, 34–36 (1938)

are said to be approximately as follows, per 1000 cubic feet of hydrogen produced

Coke	42 lbs
Steam	375 lbs
Water	1 800 gals
Fuel oil	0 5 gal (or an equivalent amount of gas)
Electric power	1 5 kw hrs
Amines	$0 005

It is to be noted that the water gas-catalytic process produces as a by product carbon dioxide equivalent to the carbon monoxide present in the original blue gas, or 400 to 450 cubic feet per 1000 cubic feet of hydrogen

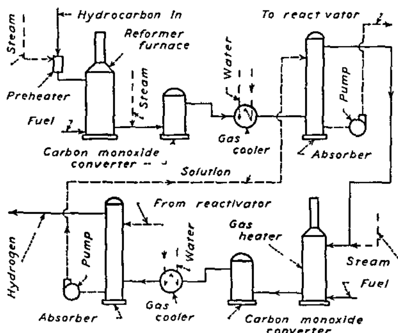


FIG 79—Hydrocarbon reforming method for the manufacture of hydrogen Girdler Corp process

(d) *The Hydrocarbon Reforming Process*

The process by which hydrogen is manufactured from natural gas butane, propane, or other hydrocarbons is quite similar to the water gas-catalytic process, inasmuch as it involves the interaction of the hydro carbons with steam at an elevated temperature over a catalyst, to crack the hydrocarbons and produce hydrogen and carbon dioxide followed by removal of the carbon dioxide by scrubbing with amines The following reaction (for the conversion of propane) is typical



$$CH_3CH_2CH_3 + 6\,H_2O = 3\,CO_2 + 10\,H_2$$

As in the water gas–catalytic process, sulfur compounds are converted to hydrogen sulfide, and scrubbed out with the carbon dioxide

Although long used in producing hydrogen for the hydrogenation of petroleum, this process has only recently been adapted to the manufacture of hydrogen of high purity for the hydrogenation of fatty oils In regions where there is a supply of natural gas without an excessive content of nitrogen it is probably the cheapest of the various hydrogen manufacturing methods It is said to also be economically attractive where propane or other liquefied hydrocarbon gases are used

(e) *Hydrogen Purification*

Hydrogen purification will be considered apart from the individual processes for hydrogen production, since the same methods of purification are applicable to hydrogen made in different ways

Carbon dioxide removal is usually effected by absorption in alkalies in scrubbing towers of either the packed or tray and bubble cap type In some plants, caustic soda is used as the alkali, the solution being merely circulated from a suitable reservoir through the tower until it is spent In other installations monoethanolamine or other amine is used as the absorbing agent, and the amine is continuously regenerated by heat Operation of the amine system of carbon dioxide removal is described in the preceding section on the water gas–catalytic method of hydrogen manufacture It is more economical than caustic soda scrubbing although in small plants charges for the use of caustic soda may not be considered excessive, even though the spent caustic is discarded after use Approximately 1 8 pounds of sodium hydroxide are required for the purification of 1000 cubic feet of hydrogen containing 1 0% of carbon dioxide, or 0 9 pound for purifying hydrogen containing 0 5% carbon dioxide

Alkali scrubbing also removes all but traces of hydrogen sulfide from the gas, but does not absorb organic sulfur compounds Traces of carbon dioxide left in the hydrogen after scrubbing are unobjectionable, since this gas is not a catalyst poison, but serves merely as a diluent in the hydrogen

At least three different methods have been used for the removal of carbon monoxide from hydrogen intended for fat hardening The system most in vogue at the present is essentially similar to the water gas–catalytic process described above, *i e* the carbon monoxide is reacted with steam at a high temperature over a catalyst to form carbon dioxide and hydrogen, after which the carbon dioxide is absorbed in an alkali

Carbon monoxide removal must be very thorough, as hydrogen containing more than a few thousandths of one per cent of this gas will markedly poison the hydrogenation catalyst in hydrogenations conducted at low temperatures In order to obtain purified hydrogen with the carbon monoxide concentration reduced to this order of magnitude, it is necessary

to conduct the water gas–catalytic operation in two or more successive stages, removing the resulting carbon dioxide after each state. In some installations the bulk of the carbon monoxide is converted in one stage, and the small residue is then catalytically converted to methane, according to the scheme outlined below.

An alternative method of carbon monoxide removal is that of methanation. In this process the hydrogen is passed through a bed of nickel catalyst maintained at a temperature of 575–600°F. The carbon monoxide is converted to methane, which is inert toward hydrogenation catalysts, according to the following equation



$$CO + 3\,H_2 = CH_4 + H_2O$$

Operation of this process is simple. A suitable catalyst is prepared by impregnating small pieces of insulating brick or other porous and refractory material with nickel nitrate, drying, and reducing the catalyst *in situ* at the operating temperature, in a current of hydrogen. The most active catalyst is obtained when reduction is rapid. An active catalyst mass will handle hydrogen equivalent to 3000 times its own apparent volume per hour, reducing the carbon monoxide content from 0.5% to about 0.001%.

One disadvantage of the methanation method of purification from carbon monoxide is that it produces another gas (methane) which cannot be easily removed from the hydrogen. Methane is not a poison for hydrogenation catalysts, but its accumulation in closed systems may be troublesome. Another disadvantage of the process is that it consumes hydrogen equivalent to three times the volume of carbon monoxide reacted. In gas containing a relatively large amount of carbon monoxide the loss of hydrogen is not a negligible item of expense. On the other hand, it has the advantage of effecting a very complete removal of carbon monoxide. The combination of a one stage water gas–catalytic purification followed by methanation thus offers the principle advantages of both systems. Complete removal of both hydrogen sulfide and organic sulfur compounds is prerequisite to successful operation of the methanation process; otherwise the methanation catalyst is rapidly poisoned and inactivated.

A third process for purifying hydrogen from carbon monoxide is the Harger-Terry preferential combustion process.[31] This process involves mixing the gas with a volume of oxygen equivalent to about twice that required for combustion of the carbon monoxide, and passing the mixture over a catalyst of iron-chromium–cerium oxides or other iron oxides at about 450°F. Under these conditions the carbon monoxide is burned preferentially to the hydrogen, so that it is almost completely converted to carbon dioxide. Steam mixed with the gas contributes to the preferential nature of the reaction.

The preferential combustion process does not produce an inert gas in

the hydrogen, but it occasions a small loss of hydrogen, and apparently does not remove the carbon monoxide as completely as methanation In addition, it involves obvious difficulties in controlling the addition and complete combustion of oxygen

Due to its extremely poisonous action toward hydrogenation catalysts, hydrogen sulfide must be completely removed from hydrogen which is to be used for fat hardening The equipment used for the removal of hydrogen sulfide from hydrogen is the same as that which has been used for many years in the manufactured gas industry, and consists of purifying boxes in which the gas is passed through a bed of iron oxide supported on wood shavings After the purifying material is saturated with sulfur, it is revivified by simply being removed and exposed to the oxidizing influence of the atmosphere The process of revivification is readily followed by observing the accompanying change in color of the material from the black of iron sulfide to the reddish color of iron oxide Since the purifying material may be re used repeatedly, the chief expense of purification is in the labor required for charging and emptying the boxes

Ordinary iron oxide treatment does not affect carbon disulfide, carbon oxysulfide, or other organic sulfur compounds in the hydrogen These are readily absorbed, however, if the iron oxide is maintained at an elevated temperature, the following equation being representative of the reactions occurring



$$CS_2 + 2\,H_2O = CO_2 + 2\,H_2S$$

At the temperatures ordinarily employed, the hydrogen sulfide is retained by the iron oxide, although if the reaction is carried out at a temperature above 300°C (572°F), it is said to remain in the hydrogen

A suitable apparatus for organic sulfur removal consists of a small box equipped with trays bearing the iron oxide supported on mineral wool The box is insulated, and in each tray are installed steam coils to maintain the temperature of the oxide in the neighborhood of 300°F The temperature is not critical however, and may be considerably higher or lower Hydrogen saturated with water vapor at ordinary temperatures carries a sufficient quantity of water for the above reaction, although it may be too dry if cooled to outside winter temperatures Since the quantity of organic sulfur in the hydrogen does not usually exceed 0 5 gram of sulfur per 100 cubic feet a single charge of oxide will suffice for the purification of a large volume of hydrogen, and operation of the process at a high temperature, in order to avoid retention of hydrogen sulfide by the catalyst, can hardly be considered worth while

7. Hydrogenation Equipment

Apparatus used for carrying out the actual reaction between hydrogen and oil may be divided into two categories, *viz* , those which operate ac

cording to the batch system, and those designed for continuous operation Of these, the former are technically by far the more important Although a tendency to replace batch with continuous processes has long been in evidence in the case of other processes, hydrogenation has presented an exception to the general trend Successful continuous hydrogenation plants were designed and placed in operation a good many years ago, but this modification of the process is still of minor importance It has been used to some extent in Europe, but it is believed that no continuous installations have been placed in operation in the United States General acceptance of the continuous process has possibly not been retarded by its failure to operate economically, as much as by the fact that it produces a hydrogenated product of quite different composition and characteristics from the batch process, continuous hydrogenation is characterized by a notable lack of selectivity, as compared with batch operation

Batch hydrogenators almost invariably employ a powder catalyst, which is suspended in the oil in a finely dispersed form during hydrogenation, and removed by filtration after the operation is completed Continuous hydrogenation systems employ a massive stationary catalyst, over which the oil is caused to flow Continuous systems employing a powder catalyst, with centrifugal separation of catalyst and oil, have been proposed, but so far as the author is aware, have not been used commercially

(a) *Batch Equipment*

As has been mentioned previously, in connection with the effect of agitation on the course of hydrogenation, the principal object in the design of a hydrogenation vessel is to obtain efficient mixing of oil and hydrogen, mixing of the catalyst–oil mass is of minor importance

During the early development of the hydrogenation process, a great variety of elaborate mixing, circulating, and spraying devices were patented, and some of these are possibly still in operation The modern tendency, however, is to employ hydrogenation equipment of comparatively simple design

Hydrogenators ordinarily consist of closed, vertical, cylindrical steel vessels, designed to withstand complete vacuum and moderate pressure, and capable of holding about 10,000 to 30 000 pounds of oil A vertical agitator is inserted through a stuffing box in the top of the vessel The agitator is preferably of the shrouded turbine type When the incoming hydrogen is injected into the housing of such a stirrer, a very efficient mixing of oil and hydrogen occurs, and the latter is expelled in the form of a fine dispersion of small bubbles, which present a large interface for absorption of the hydrogen by the oil

If the apparatus is of the "dead end" type, in which unabsorbed gas simply collects in the headspace of the vessel, a large gas–oil interface can

be maintained only if hydrogenation is rapid, since the flow of incoming hydrogen will only be equivalent to the hydrogen absorbed Such an apparatus will be much improved, therefore, if some means is provided to continuously withdraw hydrogen from the headspace and recirculate it to the hydrogen inlet line Recirculation may be provided by installing a blower in a line connecting the headspace and the inlet, or by returning the hydrogen from the headspace to the hydrogen holder to be recompressed With one type of agitator (Fig 80), some degree of hydrogen circulation within the vessel is obtained by installing a second turbine just below the oil level, and providing a suction sleeve extending into the head space, to continuously draw hydrogen into the turbine housing

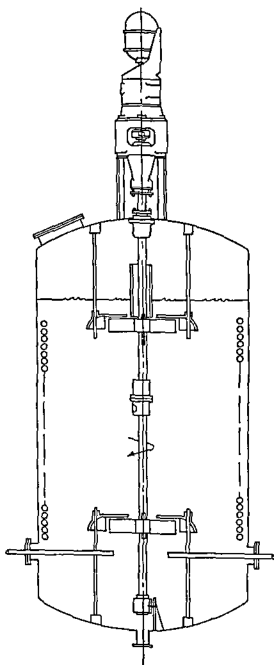


Fig 80 —Hydrogenation vessel with agitator of the internal hydrogen circulation type (design patented) (Courtesy *The Turbo Mixer Corp*)

Hydrogenators are in use which employ agitators of the propeller type, and depend upon a high degree of rolling and splashing in the headspace to promote solution of hydrogen in the oil The power requirements of such hydrogenators are excessively high, however, and they are generally less satisfactory than the type described above

Vessels for ordinary hydrogenation are usually designed for a pressure not in excess of about 75 pounds gage They are usually heated by steam at a pressure of 100 to 200 pounds Steam coils installed for heating are usually used also for the circulation of cooling water The hydrogenated oil must of course be cooled before it is filtered, and means must also be provided for controlling the tempera

ture of the oil during the course of the reaction, which is exothermic A necessary accessory of a hydrogenation plant is a vacuum pump, to exhaust air from the headspace of the hydrogenators before hydrogenation is started, and to maintain a vacuum while the finished batch is cooled An atmosphere of hydrogen may of course be maintained over the oil during the cooling period, or while the oil is pumped out of the vessel through a heat exchanger, but more precise control of the hydrogenation is obtained if the reaction is stopped sharply at the desired point by blowing off the hydrogen from the headspace and immediately placing the batch under a vacuum

(b) *Continuous Equipment*

The continuous hydrogenation process developed by Bolton and Lush[36] employs a catalyst consisting of nickel turnings enclosed in a cylindrical cage of metal screen The cages are encased in cylinders, through which the oil is pumped continuously, in an atmosphere of hydrogen The surface of the catalyst is rendered catalytically active by first forming upon it a coating of oxide by "anodic oxidation," and then reducing the oxide back to the metal at a relatively low temperature In the process of anodic oxidation, the cage and its contents are made the anode in an electrolytic bath employing sodium carbonate as an electrolyte Passage of a direct current for a suitable period, followed by thorough washing of the catalyst, places the latter in condition to be reduced to an active form After the catalyst has become inactivated in use it is restored to its original activity by extraction with a solvent and repeated anodic oxidation and reduction

Two methods are described for operation of the Bolton-Lush apparatus It may be operated by the "drip" method, in which the oil is allowed to drip down the catalyst mass, without flooding of the latter, or by the "over flow" method, in which the catalyst chamber is filled with oil at all times The drip method yields a product very low in iso oleic acid, but nonselectively hydrogenated In operation by the overflow method somewhat greater selectivity is obtained, but the production of iso oleic acid is very high

An active catalyst mass consisting of 10% metal and 90% voids, is said to be capable of hydrogenating cottonseed oil to an iodine value of 50 at a rate equivalent to its own weight each hour

8 Hydrogenation in Practice

(a) *Effect on the Characteristics of Oils*

The characteristic of oils most directly affected by hydrogenation is the iodine value, which decreases in direct proportion to the amount of

[36] E R Bolton *J Soc Chem Ind* 46, 444–446T (1927) E J Lush *ibid*, 42, 219–225T (1923) L H Manderstam *Oil & Soap*, 16, 166–172 (1939)

hydrogen added. Characteristics which do not depend upon the unsaturation of the oil, such as the saponification value, hydroxyl value, Reichert-Meissl value, content of unsaponifiable matter, etc., are substantially unchanged by hydrogenation.

Ordinarily the free fatty acid content of an oil does not change to any extent during hydrogenation. However, some catalysts, such as the nickel sulfate–sodium bicarbonate catalyst described in a previous section, are inclined to slightly hydrolyze the oil, and may increase the fatty acid content by as much as 0.1–0.3%, if the hydrogenation is prolonged, and conducted at a high temperature.

Certain nonglyceride constituents of vegetable oils are reduced in the process of hydrogenation. Carotenoid pigments are markedly bleached. Unbleached palm oil, which is naturally of a very deep orange red color, is no darker than ordinary vegetable seed oils after hydrogenation. The color of bleached cottonseed oil, peanut oil, soybean oil, etc. is often reduced by as much as 50%. There is some evidence that the increased stability of oils which have been hydrogenated may be due to the development of antioxidants by hydrogenation (as for example by the reduction of quinones to hydroquinones) as well as to reduction of the unsaturation of the oils.

Hydrogenation tends to destroy the natural odors and flavors of fats and oils, substituting in their place a distinctive "hydrogenation odor," which must be removed from edible fats by deodorization. The constituents responsible for this odor are unknown, but they are evidently developed from glycerides rather than impurities in the oil, since all oils and fats tend to develop similar odors.

The stability of oils, as measured by the Swift test or other accelerated tests, is progressively increased as the oils are hydrogenated. The effect of hydrogenation varies somewhat with both the nature of the oil and the conditions of hydrogenation, but in the case of peanut, cottonseed or soybean oils hydrogenated with reasonably good selectivity, there is an approximately linear relationship between the iodine value of the oil and the logarithm of the keeping time, down to an iodine value of about 50, with the stability doubling each time that the iodine value is reduced 7 to 15 units.

Hydrogenation reduces the refractive indices of oils, each variety of oil having a more or less characteristic iodine value–refractive index curve dependent upon the average molecular weight of its fatty acids. The relationship between refractive index and iodine value is very nearly the same for many vegetable oils (Fig. 81), although rapeseed oil, which is high in molecular weight, and coconut type oils, which are low in molecular weight, deviate quite markedly from the average. The correlation between iodine value and refractive index is not precise for any given variety

of oil, but the refractive index will generally serve to indicate the iodine value of a hydrogenated oil within one or two units Since refractive index measurements may be easily and quickly made, they are often used as means of controlling the hydrogenation However, an actual iodine value by the rapid method of Hoffman and Green[37] can be determined about as quickly, and it of course gives a closer indication of the progress of hydrogenation

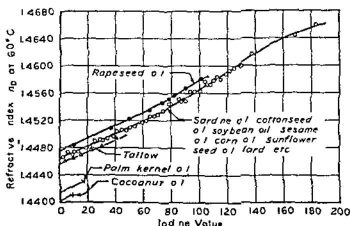


FIG 81 —Iodine value *vs* refractive index for various hydrogenated oils

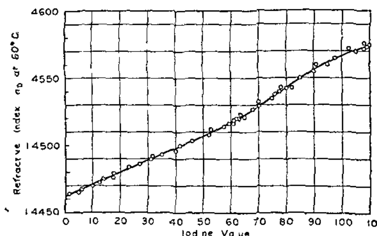


FIG 82 —Iodine value *vs* refractive index for hydrogenated cottonseed oil

During the first stages of hydrogenation, the consistency of an oil, and its characteristics related to consistency, such as melting point, softening point, congeal point, etc , depend a great deal upon the conditions of hydrogenation For example, if the consistency is measured by the micropenetration method outlined by Feuge and Bailey,[38] the micropenetration

[37] H D Hoffman and C E Green, *Oil & Soap*, **16**, 236–238 (1939).
[38] R O Feuge and A E Bailey, *Oil & Soap*, **21**, 78–84 (1944)

at 22 5°C (72 5°F) of cottonseed oil hydrogenated to an iodine value of 65 may be as low as about 25 or as high as about 125, according to the amounts of saturated and iso oleic acids in the sample In the later stages of hydrogenation, the percentage of saturated acids in the oil becomes a function simply of the iodine value of the oil, and the percentage of iso-oleic acid is not greatly different under different conditions of hydrogenation, so that the melting point, etc are quite predictable from the iodine value Typical curves of iodine values *vs* melting point and titer, for various highly hydrogenated oils, are reproduced in Figs 83 and 84 The titer of hydrogenated cottonseed oil exhibits the peculiarity of passing through a minimum at an iodine value between 80 and 85 (Fig 85)

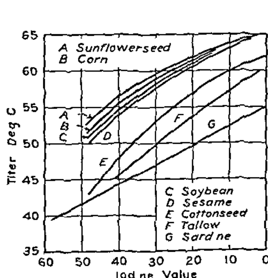


FIG 83 —Iodine value *vs* titer (in degrees C) for various hydrogenated oils

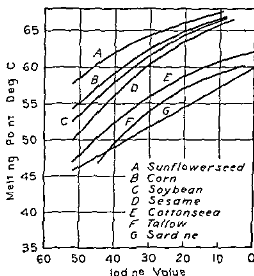


FIG 84 —Iodine value *vs* melting point (closed capillary) for various hydrogenated oils

The typical alteration of consistency with hydrogenation is illustrated in the case of different oils in the micropenetration curves of Figures 86 and 87

(b) *Hydrogenation of Stearine or Hard Oils*

Hydrogenated stearines, or hard oils are principally manufactured for use in making blended type shortenings, or for stiffening soft lards They may also be desired as raw materials for the production of stearic acid, however, or for a variety of other purposes The terms "vegetable stearine" and "animal stearine" are applied respectively to vegetable and animal oils or fats which have been hydrogenated to a brittle consistency and an iodine value usually less than about 20 The stiffening capacity of

a hard oil is very closely measured by its titer Vegetable stearine was originally prepared as a substitute for oleostearine, which has a titer of

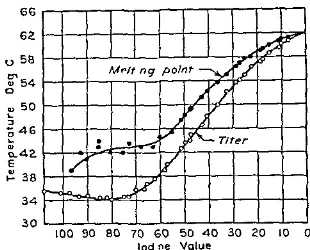


FIG 85—Iodine value vs titer and melting point (closed capillary) of hydrogenated cottonseed oil

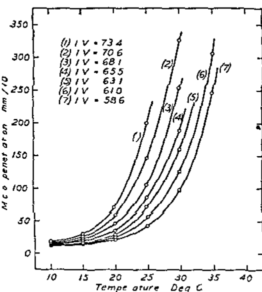


FIG 86—Micropenetrations of cottonseed oil hydrogenated to different degrees (typical curves) [33]

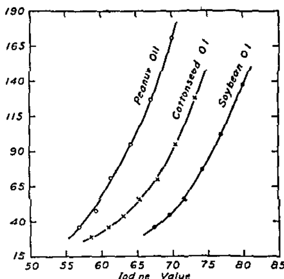


FIG 87—Typical variations in consistency of different oils with hydrogenation Micropenetration at 22 5° C (mm /10) vs iodine value of the oils [33]

about 50°C, and must be mixed with cottonseed oil in the ratio of about 20 parts to 80 to produce a shortening of the proper consistency However, it is now customary to hydrogenate vegetable oils to a titer of about

58° or above, not more than about 10% of such a hard oil is required in a blended shortening Some oils can be hardened to considerably higher titers than others (Fig 83)

The hydrogenation of stearine is the least critical of all hydrogenation operations, such considerations as selectivity and iso oleic acid suppression are naturally unimportant in the manufacture of this product If a catalyst is to be used only for hard oil production, it may be selected purely on the basis of its activity In order to make the reaction as rapid as possible, the highest possible pressure is usually used, and the temperature is often allowed to rise as high as 400°F., or even higher At high temperatures and pressures, it may be that the rate at which hydrogenation can be conducted will depend upon the capacity of the cooling coils in the hydrogenator for carrying away the heat of the reaction, which is strongly exothermic Ordinarily about 3 to 4 hours will be required to reduce cottonseed oil to an iodine value of 10 and a titer of 60°C, at a pressure of 60 pounds gage, a maximum temperature of 400°F, and a catalyst concentration equivalent to 0 03–0 04% nickel If only fresh catalyst is used the best results will be obtained by reserving a portion of the catalyst to be added toward the end of the hydrogenation e g, 0 02% may be added to the hydrogenator at the beginning of the run, and 0 01% may be added after the iodine value is reduced to about 30 or 40 Catalyst which has been partially inactivated in the manufacture of other products may be used to good advantage in making hard oil, although some catalysts are inclined to produce excessive amounts of free fatty acids in the oil, if so used in high concentrations

In the manufacture of hard oil, as in all other hydrogenations, the operation is best controlled by periodically drawing samples from the hydrogenator, estimating the iodine value, either directly, by a quick method, or indirectly, from the refractive index, and plotting the iodine value against the hydrogenation time If this is done, and the relation between iodine value and titer is known, it is a simple matter to determine the point at which the desired titer will be reached by extrapolating the time–iodine value curve

(c) *Hydrogenation of Shortenings*

In the shortening trade in the United States all hydrogenated shortenings constitute a distinctive class of high grade products, which are manufactured to rigid standards of color, free fatty acid content, flavor and odor, stability, consistency, etc They are hydrogenated in such a manner as to obtain the lowest iodine value and the highest stability that is consistent with the proper consistency Quite definite iodine value standards are generally recognized for products intended for bakery consumption They are about 60 to 65 for shortening made from cottonseed oil, and about 70 or 75 for shortening made exclusively from soybean oil Comparable

shortenings made from peanut oil alone have not as yet appeared upon the market in quantity, but presumably they would have iodine values somewhat lower than those of cottonseed oil shortenings

Iodine values such as those listed above are obtained by so adjusting the hydrogenation conditions as to minimize the formation of iso oleic acid and at the same time obtain reasonably good selectivity and prevent the formation of excessive amounts of saturated acids This adjustment is a somewhat delicate matter, since conditions leading to high selectivity and low iso oleic acid formation are to some extent mutually exclusive

Conditions suitable for the hydrogenation of all hydrogenated shortenings can hardly be stated categorically, due to differences in agitation in different hydrogenators, and variations in catalyst activity However, in general it may be said that these conditions will be about as follows pressure, 10 to 60 pounds, gage, temperature, 200° to 300°F , and catalyst concentration, 0 05% to 0 10% nickel Some hydrogenators prefer to conduct the operation in successive steps at two different temperatures, employing a low temperature in the first stage to minimize iso oleic acid formation and a high temperature in the second stage to reduce the percentage of linoleic acid

All hydrogenated shortenings of the biscuit and cracker type are prepared similarly to regular all hydrogenated shortenings, except that the hydrogenation is conducted more selectively These shortenings have insufficient saturated acids to give them a good high temperature body, but they are very low in linoleic acid and correspondingly high in stability

The operating and analytical data contained in Table 156 may be considered more or less representative of good practice with an active, fresh, catalyst, purified steam–iron hydrogen, and hydrogenation equipment employing efficient agitation Of the samples in this table, *1* and *3* may be considered good examples of standard all hydrogenated shortening, and *2* may be considered typical of biscuit and cracker shortenings

It will be found in practice that different batches of hydrogenated oil will inevitably vary slightly in composition and characteristics, even though they may all be hydrogenated to precisely the same iodine value The characteristic most urgently required by shortening consumers is uniformity in body in the neighborhood of 70–75°F , hence it is advisable to hydrogenate all batches to the same consistency within this range of temperature and permit slight variations in iodine value and stability If a large number of batches are prepared in a plant during each day, and these are mixed, the individual batches may permissibly exhibit considerable variation, provided that the average consistency does not vary from day to day The problem of control is more difficult if operating conditions are such that it is not possible to adjust the body of the finished product by suitable blending of hard and soft batches In the latter case, it is almost essential to interrupt the hydrogenation at some point slightly

short of the degree of hydrogenation eventually desired, draw a sample, and check the consistency of the fat before finishing the batch As a control method for this check the quick micropenetration method described by Feuge and Bailey[38] is recommended Some hydrogenators employ the setting point or congeal point as a method of control during the hydrogenation of shortenings It may be mentioned that shortenings prepared by blending hard and soft stocks are never quite as low in iodine value as shortenings of equivalent body prepared by straight hydrogenation

TABLE 156

ALL-HYDROGENATED SHORTENINGS MADE FROM COTTONSEED OIL ANALYSES OF TYPICAL PRODUCTS MADE UNDER DIFFERENT HYDROGENATION CONDITIONS

Conditions and analyses	Sample number			
	1	*2*	*3*[a] First stage	*3*[a] Second stage
Hydrogenation conditions				
Temperature, °F	218	275	165	250
Pressure, lbs /sq in gage	50	50	50	50
Catalyst, % nickel	0 07	0 10	0 07	Same
Hydrogenation time, min	175	63	130	25
Iodine value at end of hydrogenation period	63 8	62 8	75	62 5
Composition of fatty acids, finished shortening				
Saturated, %	32 7	28 8	33 0	
Iso-oleic, %	10 2	14 0	8 1	
Oleic, %	50 7	55 4	53 9	
Linoleic, %	6 4	1 8	5 0	
Micropenetrations of finished shortening, mm /10, at				
45°F	15	13	15	
70°F	55	55	55	
85°F	165	180	130	
98°F	340	Almost melted	320	
Stability, by Swift method, hrs	75	200	98	

[a] Hydrogenation conducted in two stages

Although all-hydrogenated and blended shortenings formerly comprised two entirely distinct types, hydrogenation has lately been extended to so many different products that from the manufacturing standpoint the distinction is no longer clear cut Many shortenings marketed in the blended shortening price class are actually prepared by a combination of blending and hydrogenation In making blended shortenings containing both cottonseed oil and soybean oil, for example, it is quite common practice to stabilize the soybean oil against flavor reversion by hydrogenating it to a maximum degree, while the more stable cottonseed oil may be hydrogenated little, if at all Shortenings containing tallow, as well as other

blended shortenings, are often slightly hydrogenated after blending, to the extent of 1 to 10 units decrease in iodine value

The hydrogenation of blended shortenings is naturally much less critical than that of shortenings of the all hydrogenated type It is usually carried out at a relatively high temperature, with catalyst which has previously been used in the hydrogenation of other products

(d) *Hydrogenation of Margarine Oils*

The hydrogenation of margarine oils, like that of all hydrogenated shortenings, is a highly critical process, although the characteristics desired in the finished products are somewhat different In the case of shortenings, it is desirable for the products to be as soft and plastic at the lower temperatures as is feasible, and at the same time have some body at a temperature in the neighborhood of 98°F Margarine oils must be quite hard at refrigerator temperatures, in order to simulate the consistency of butter, and in order that the margarine may be formed and packaged in the customary prints, but at the same time they must melt completely at the temperature of the human body, in order to not be "pasty" in the mouth

TABLE 157

MARGARINE OIL MADE BY THE HYDROGENATION OF COTTONSEED OIL

OPERATING AND ANALYTICAL DATA

	275
	5
Catalyst, % nickel	0 08
Hydrogenation time min	230
Iodine value	67 0
Composition of fatty acids	
Saturated %	26 5
Iso oleic, %	20 8
Oleic %	48 2
Linoleic, %	4 5
Micropenetrations, mm /10, at	
45°F	15
70°F	65
80°F	140
90°F	295
98°F	Melted
Congeal point, °C	26 2

The desired characteristics in margarine oil prepared from cottonseed or similar oils are obtained by choosing hydrogenation conditions which will produce much iso oleic acid, but almost no saturated acids Typical operating and analytical data covering the preparation of margarine oil from cottonseed oil are given in Table 157 It will be noted that the hydrogenation conditions listed in this table are similar to those of *2*, Table 156 (biscuit- and cracker-type all hydrogenated shortening), except

etc , is used in the powder form, and agitation of the catalyst and reacting material is accomplished by circulation of the hydrogen

Relatively high yields of alcohols are obtained, thus, for example, in the laboratory Adkins and Folkers[42] obtained yields of alcohols from the esters as high as 97 5–98 5%

Ordinarily the reaction is not selective with respect to the reduction of carboxyl groups, *i e*, unsaturated acids are hydrogenated to the corresponding saturated acids at the same time that hydrogenation of the carboxyl groups is accomplished Under certain conditions, however, it may be reasonably selective For example, Sauer and Adkins,[49] using a zinc chromite catalyst and a very high ratio of catalyst to fatty material, were able to obtain a 68% yield of unsaturated alcohols from oleic acid esters

The use of alloy steel reactors is necessary in the hydrogenation of fatty materials to alcohols, to avoid corrosion of the equipment and metallic contamination of the product

A somewhat different method of operation is employed in the so called lead soap process, which is covered by a series of patents issued to Richardson and Taylor [50] In this process the fatty acids are reacted with litharge to form lead soaps, and the latter are then treated with gaseous hydrogen, without the use of an additional catalyst, at a pressure in the neighborhood of 4000 pounds per square inch, and at a temperature in excess of 300°C (*e g*, 340°C) Reaction occurs to produce alcohols in both the free and esterified forms, according to the following equations



$$(RCOO)_2Pb + 5\ H_2 \rightarrow 2\ RCH_2OH + 2\ H_2O + Pb \qquad \text{and}$$



$$(RCOO)_2Pb + 3\ H_2 \rightarrow RCOOCH_2R + 2\ H_2O + Pb$$

The lead is recovered in molten, metallic form In a typical example given in one of the patents the reaction mixture from the treatment of lead oleate consisted of less than 1% oleic acid, about 21% oleyl oleate, and about 77% free oleyl alcohol The product had an iodine value of 81, indicating that about 85% of the double bonds of the oleic acid had escaped saturation

The lead soap process appears particularly desirable for the preparation of unsaturated fatty alcohols Alternatively to lead, various other metals, notably cadmium, may be employed for forming the lead soaps, although less satisfactorily The process is adaptable to continuous operation

(b) *Fatty Alcohols by Sodium Reduction*

The classical Bouveault-Blanc[51] method for producing fatty alcohols from the corresponding fatty acids by sodium reduction may be con

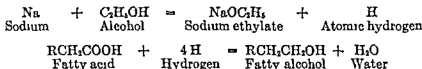
[49] J Sauer and H Adkins, *J Am Chem Soc*, 59, 1–3 (1937)

[50] A S Richardson and J E Taylor (to Procter & Gamble Co), U S Pats 2 340 343–44 and 2 340,687–91 (1944)

[51] L Bouveault and G Blanc, *Compt rend*, 136, 1676–1678 (1903)

sidered a variant of the hydrogenation process, inasmuch as the sodium serves merely to liberate atomic hydrogen from the alcohol used in the reaction, hydrogenation then proceeding in a manner similar to that indicated above in catalytic hydrogenation

The reactions are as follows



Na	+	C_2H_5OH	=	$NaOC_2H_5$	+	H
Sodium		Alcohol		Sodium ethylate		Atomic hydrogen

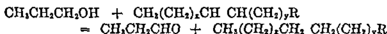
RCH_2COOH	+	4 H	=	RCH_2CH_2OH	+	H_2O
Fatty acid		Hydrogen		Fatty alcohol		Water

Sodium reduction has been and is still used on a commercial scale for the production of fatty alcohols It has the advantage over catalytic hydrogenation of effecting no change in the unsaturation of the fatty acid chain, hence is particularly desirable for the manufacture of products containing a high proportion of unsaturated alcohols

In commercial practice, the higher alcohols, *e g* methyl cyclohexanol, are employed for the process, because they have the advantage over ethyl alcohol of being safer to use and more easily recovered

(c) *Conjugated Hydrogenation*

Conjugated hydrogenation refers to that variation of the hydrogenation process wherein the hydrogen is not supplied in a gaseous form, but is contributed by an alcohol, the alcohol being converted to an aldehyde in the process The following reaction of a fat with propyl alcohol is typical



$$CH_3CH_2CH_2OH + CH_3(CH_2)_xCH\ CH(CH_2)_yR$$
$$= CH_3CH_2CHO + CH_3(CH_2)_xCH_2\ CH_2(CH_2)_yR$$

This process, so far as is known, has not attained technical importance, but it has been the subject of a considerable amount of investigation by Russian workers[52, 53]

Although in conjugated hydrogenation, as in ordinary hydrogenation, the composition of the hydrogenated fat is presumably influenced by the conditions of hydrogenation, the published analyses of hydrogenated oils would indicate that the method is inclined to be relatively selective, and to produce large proportions of iso oleic acids The following compositions were reported by Rush, Dvinianinkova, and Liubarskii[53] for sunflower oil hydrogenated at 260°C with propyl alcohol and a nickel catalyst

Saturated acids	12 5–14 8%
Oleic acid	50 8–56 3%
Iso oleic acid	22 0–33 1%
Linoleic acid	3 6–10 3%

[52] E I Liubarskii, *J Applied Chem U S S R*, **5**, 1025–1045 (1932)

[53] V A Rush, I L Dvinianinkova and E I Liubarskii, *J Applied Chem U S S R*, **10**, 702–708 (1937)

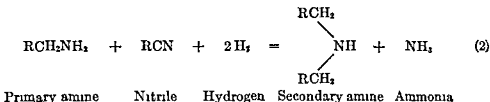
(d) Hydrogenation of Nitriles Derived from Fatty Acids

A hydrogenation process of some technical importance is the hydrogenation of nitriles derived from fatty acids, to form amines. The process is carried out with a nickel or cobalt catalyst at temperatures and pressures which have not been made generally known.

Ordinarily both primary and secondary amines are produced, according to the following equations:



$$\underset{\text{Nitrile}}{RCN} + \underset{\text{Hydrogen}}{2H_2} = \underset{\text{Primary amine}}{RCH_2NH_2} \qquad (1)$$



$$\underset{\text{Primary amine}}{RCH_2NH_2} + \underset{\text{Nitrile}}{RCN} + \underset{\text{Hydrogen}}{2H_2} = \underset{\text{Secondary amine}}{(RCH_2)_2NH} + \underset{\text{Ammonia}}{NH_3} \qquad (2)$$

However, a maximum production of primary amines is generally desired, the secondary amines being merely an undesirable by-product. Production of secondary amines may be inhibited by the addition of gaseous ammonia to the hydrogenator at the beginning of the reaction, and the maintenance of a substantial pressure of ammonia relative to that of hydrogen as hydrogenation progresses.[54] It is claimed by Young and Christensen[55] that further improvement in the yield of primary amines, e. g., from about 50% to 70–80%, is obtained by the addition of water and caustic soda or other alkaline substance to the nitriles before the latter are hydrogenated.

[54] A. W. Ralston, *Oil & Soap*, **17**, 89–91 (1940).

[55] H. P. Young and C. W. Christensen (to Armour & Co.), U. S. Pat. 2,287,219 (1942).

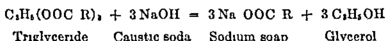
CHAPTER XIX

SOAPMAKING

1. The Saponification Process

(a) *Chemistry and Physical Chemistry of the Soap Kettle*

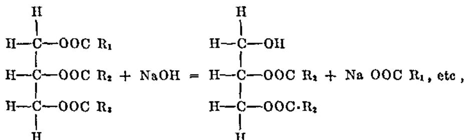
The over-all reaction occurring in the saponification of a fat with caustic soda[1] may be represented as follows



$$C_3H_5(OOC\cdot R)_3 + 3\,NaOH = 3\,Na\cdot OOC\cdot R + 3\,C_3H_5OH$$

Triglyceride Caustic soda Sodium soap Glycerol

Although the reaction may occur in successive stages:



$$\begin{array}{c} H \\ | \\ H—C—OOC\cdot R_1 \\ | \\ H—C—OOC\cdot R_2 \\ | \\ H—C—OOC\cdot R_3 \\ | \\ H \end{array} + NaOH = \begin{array}{c} H \\ | \\ H—C—OH \\ | \\ H—C—OOC\cdot R_2 \\ | \\ H—C—OOC\cdot R_3 \\ | \\ H \end{array} + Na\cdot OOC\cdot R_1, \text{ etc.,}$$

it has been shown by Kellner[1a] that there is no accumulation of mono- or diglycerides in the reaction mass at any stage of the saponification process Fatty acids, unlike fats, may be saponified with sodium or potassium carbonate, as well as with caustic soda or caustic potash Saponification with caustic potash or potassium carbonate is entirely analogous to saponification with caustic soda and sodium carbonate

Saponification is commonly brought about by boiling the fat with strong lye in an open kettle Since neutral fat and aqueous alkali solution are immiscible, the reaction rate is at first slow, and principally dependent

[1] For detailed treatment of the physical chemistry of soapmaking, see J W McBain in *Colloid Chemistry*, Vol I, edited by Jerome Alexander, Chemical Catalog Co , New York, 1926, and also the many original articles by McBain and co-workers See also R H Ferguson, *Oil & Soap*, **9**, 5–8, 25 (1932), and R H Ferguson and A S Richardson, *Ind Eng Chem* , **24**, 1329–1236 (1932) The practical aspects of soapmaking are covered in such treatises as those of G Martin, *The Modern Soap and Detergent Industry*, 2nd ed , Lockwood, London, 1931, E G Thomssen and C R Kemp, *Modern Soapmaking*, MacNair-Dorland Co , New York, 1937, and A Kufferath, *Die Seifenherstellung*, Hartleben, Vienna, 1942

[1a] J Kellner, *Chem Ztg* , **33**, 453 (1909)

upon the magnitude of the interface between the two liquids In the later stages, however, saponification may be considered an essentially homogeneous reaction, proceeding through concurrent solution of fat and alkali in a phase consisting of preformed soap The reaction, therefore, is markedly autocatalytic If the amount of fat saponified is plotted against reaction time, a sigmoid curve results, the reaction, at first slow, accelerates rapidly as increased quantities of soap are formed, and slows again only toward the end, as the concentration of fat becomes low, and considerable proportions of fat tend to become occluded amongst alkali improverished soap micelles The marked ability of strong soap solutions to dissolve neutral fats and the significance of this phenomenon in soap making was *perhaps first pointed out by Smith,*[2] *and is now generally recognized*[3]

In technical practice, soap is often boiled on a niger of preformed soap left from a previous boil Fresh fat and alkali slowly added to the boiling soap mass is believed to saponify almost instantly Considerable heat (about 65 cal per kg fat saponified) is evolved in the reaction, hence the addition of fat and lye must be carefully controlled to avoid boiling the batch out of the kettle from the excessively rapid generation of heat

Since free fatty acids react more readily with alkali than do glycerides, a fat charge containing some proportion of free fatty acids is saponified more readily than one which is substantially neutral Fats of a relatively low degree of unsaturation saponify more readily than more highly unsaturated fats

The complete series of operations in the manufacture of a batch of full boiled or settled soap is as follows (*a*) Reaction of the fat with alkali in one or more successive stages, with the incompletely saponified soap mass being "grained out" by the addition of salt or brine after each stage (The aqueous solution remaining after separation of the insoluble soap curd is retained for the recovery of glycerol) (*b*) Boiling of the redissolved soap with lye to complete saponification, and graining out of the completely saponified soap mass with lye (*c*) *Separation of the completely saponified* soap mass into immiscible phases of niger and neat soap, by boiling with the addition of water and salt—the so called "pitching" or "fitting" operation The neat soap resulting from this operation is the product used in making the various soaps of commerce

The physicochemical nature of soaps and soap solutions has been discussed at some length in a previous chapter (pages 328–338), hence it is necessary here to consider only the system of soap, water, and electrolyte existing at approximately 100°C in the soap kettle Such a system is represented in the diagram of Figure 88 In the present discussion this diagram is intended to be illustrative only, although the phase boundaries

[2] E L Smith, *J Phys Chem* **36**, 1401–1418 (1932)

[3] See, for example, L Lascaray, *Fette u Seifen*, **46**, 531–536 (1939)

have been placed as accurately as possible, according to the data of Ferguson[4] and Ferguson and Richardson[5] for tallow soap The various operations in soap boiling are best explained with reference to this diagram.

As explained in a previous chapter (page 329), the use of phase diagrams for commercial soaps is fully justified, as the work of McBain, Ferguson, and others has shown that these soaps behave essentially like salts of single fatty acids, with negligible fractionation of the individual components occurring upon separation of the soap into two phases or partial transformation of the soap from one phase to another

In Figure 88 are represented equilibrium conditions at 100°C in a system composed of tallow soap, water and sodium chloride, with the percent by weight of anhydrous soap being plotted along the vertical axis, and percent

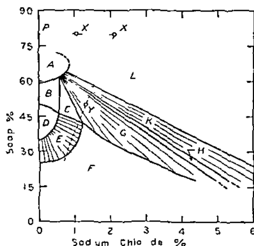


Fig 88 —Illustrative diagram, soap–water–salt system (*A*) Neat soap, (*B*) neat middle, (*C*) neat–middle–niger (*D*) middle, (*E*) middle–niger, (*F*) niger, (*G*) neat–niger, (*H*) neat niger–lye, (*K*) neat–lye (*L*) curd–lye

by weight of sodium chloride plotted along the horizontal axis Thus the composition of any combination of soap, water, and salt can be represented by a single point within the area bounded by the two axis and 100% concentration respectively of soap and salt While but one electrolyte, sodium chloride, has been represented, the effect of mixed electrolytes in such systems is additive,[6] hence the diagram may also be considered to indicate the action of caustic soda or mixtures of caustic soda and salt, calculated in terms of sodium chloride The minor amounts of glycerol which may be present in the system during actual soap boiling operations, are unimportant in the present connection, and for purposes of discussion may be neglected entirely

[4] R H Ferguson *Oil & Soap* 9, 5–8, 25 (1932)
[5] R H Ferguson and A S Richardson, *Ind Eng Chem* 24, 1329–1336 (1932)
[6] J W McBain and A V Pitter, *J Chem Soc*, 1926, 893–898

The portion of the diagram which is of importance in soap boiling is that representing a soap concentration of about 50–70%, and a salt concentration of about 0–4%, and comprising the upper portions of areas *C*, *G*, *H*, *K*, and *L*. Each of the "salting out" operations brings the system into area *L*, consisting of immiscible lye or brine, and grainy or curd soap. After the final salting out with lye is completed, and the lye is withdrawn from the completely saponified curd soap, the latter consists of a somewhat ill defined mixture of hydrated curd and occluded lye, which may, for example, have the total composition represented by point *X*. The object of the finishing or pitching operation is to bring the composition of the system to a point within area *G*, as for example, to point *Y*. At this point the batch will separate into two phases consisting respectively of neat soap and niger. The composition of the two separated phases is represented by the ends of the tie line passing through point *Y*. In this case, the neat soap and the niger will contain about 62% and 30%, respectively, of anhydrous soap. The chief object of this separation, it may be mentioned, is to purify the soap, the niger retains most of the coloring materials and other undesirable impurities of the fat. It is very important to attain the proper proportions of neat soap and niger. If too much soap is included in the neat phase, and too little in the niger, purification will be short of that desired. On the other hand, the production of an unnecessarily large niger will diminish the yield of finished soap and create a problem in disposing of the soap in the niger phase.

All compositions obtainable by the simple addition of water lie on a line drawn from *X* to the origin, hence it is apparent that the composition represented by *Y* cannot in this case be attained by adding water alone, but must be reached by diluting the mass with water, and at the same time adding a sufficient amount of electrolyte to bring the composition of the system into alignment with the line *X'O*.

The very narrow limits within which the soapmaker must work are evident from the diagram. The addition of but slightly too small an amount of water will produce too small a niger, the addition of a very slight excess of water will make the niger too large. Further, by the addition of water not greatly in excess of the proper amount, or by failure to thoroughly mix in the water as it is added, the system may be brought into regions *C* or *E*, with the formation of middle soap. This form of soap appears during soap boiling in the form of undesirable gummy lumps or masses, which are very troublesome to eliminate, once they are formed.

The phase boundaries are considerably altered by changes in the composition of the fat. The comparative phase diagrams of Ferguson and Richardson[5] for tallow soap, coconut oil soap, and mixtures of the two are shown in Figures 89, 90, 91, and 92. Considering the necessity for pre-

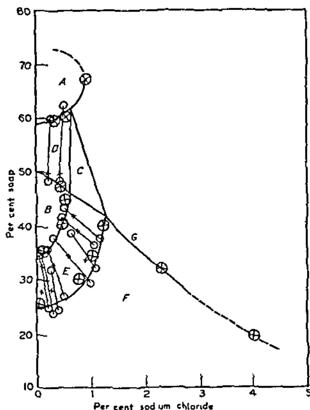


FIG 89 —Phase diagram for tallow soap (*A*) Neat soap, (*B*) middle soap, (*C*) neat-middle-niger, (*D*) neat-middle, (*E*) middle-niger, (*F*) niger, (*G*) neat-niger [5]

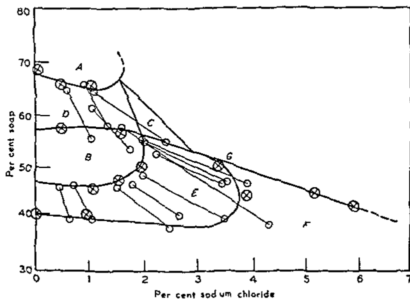


FIG 90 —Phase diagram for coconut oil soap (*A*) Neat soap, (*B*) middle soap, (*C*) neat-middle-niger, (*D*) neat-middle, (*E*) middle-niger, (*F*) niger, (*G*) neat-niger [5]

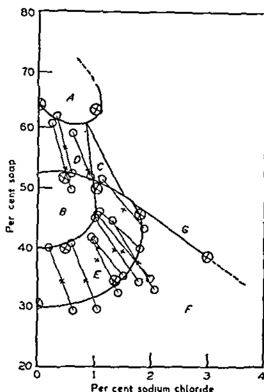


Fig 91 —Phase diagram for 75% tallow–25% coconut oil soap (*A*) Neat soap, (*B*) middle soap, (*C*) neat-middle-niger, (*D*) neat-middle, (*E*) middle-niger, (*F*) niger, (*G*) neat-niger [5]

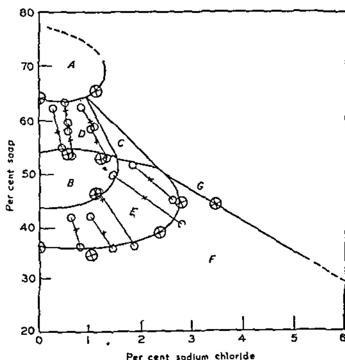


Fig 92 —Phase diagram for 50% tallow–50% coconut oil soap (*A*) Neat soap, (*B*) middle soap, (*C*) neat-middle-niger, (*D*) neat-middle, (*E*) middle-niger, (*F*) niger, (*G*) neat-niger [5]

cisely determining the composition of the batch in order to make the pitching operation successful, and the variability in phase boundaries occasioned by unavoidable variations in the fat, it is understandable that soapmaking cannot be readily reduced to a series of mechanical operations, but must depend upon the skill and judgement of the experienced soap maker, who is able to closely judge the progress of the operation by the appearance of the batch

From the relatively narrow range of soap concentrations in which the tie lines of area *G* intersect the lower boundary of area *A* (Fig 88), it is evident that the soap content of different batches of neat soap from a given stock cannot vary greatly in composition In the case of tallow soap, the possible variation in anhydrous soap content is from about 62–63% (The soap content of commercially made neat soap is about 2% higher) The anhydrous soap content of neat soap from coconut oil is somewhat higher, *i e*, about 67–69% (Fig 90) It is to be noted from Figures 89 to 92 that the areas of homogeneity and heterogeneity of the different soap phases extend over progressively wider concentrations of electrolyte as the percentage of coconut oil in the fatty stock increases It is pointed out by the above mentioned authors that this effect makes the accidental formation of middle soap more likely in the case of stocks containing large proportions of coconut oil than in the case of ordinary stocks

(*b*) *Soap Boiling*

Soap boiling is carried out in large cylindrical kettles equipped with conical bottoms, steam coils, and delivery pipes for lye, water, and brine The latter are preferably placed so as to spray the liquid more or less uniformly over the entire surface of the kettle A swinging "skimmer" pipe is provided for drawing off the neat soap from the niger In the larger plants, soap kettles may have capacities as high as 500,000 pounds They are usually suspended through the operating floor, projecting through this floor sufficiently for the soap boiler to conveniently observe the contents Some plants use kettles clad with nickel or nickel alloys, to avoid contamination of the soap with iron

The following is intended to describe the operation of soap boiling in a general way, and is of course not intended to constitute a manual for the operation of this difficult process

Since the choice of fatty materials for soapmaking has been discussed in a previous chapter, it will only be repeated here that the principal considerations are the provision of a fat mixture containing saturated and unsaturated, and long and short chain fatty acids in suitable proportions to yield the desired qualities of hardness, solubility, ease of lathering, etc , in the finished product, and sufficient refining and bleaching of the fat charge to insure a good appearance A very common mixture for the

manufacture of toilet soaps is about 75% tallow and 25% coconut oil To produce a white toilet soap of sufficiently light color Thomssen and Kemp[7] recommend that the color of the tallow be not darker than 3 on the FAC scale, and that the coconut oil have a Lovibond color not in excess of 10 yellow and 2 red

If a full boiled soap is to be made, the process is carried out in a series of operations termed "changes," each of which is terminated by graining out the soap and drawing off from beneath it an aqueous solution of glycerol, lye, salt, etc The final operation, in which the soap is separated into neat soap and niger, is known as "finishing," "fitting," or "pitching"

In order to obtain a maximum recovery of glycerine, and also to wash the soap as free as possible of impurities, the actual saponification is usually carried out in at least three successive changes In the first of these a portion of the fat charge is boiled with strong lye or caustic soda solution (*e g*, 30° Bé) The proportions of lye and fat are adjusted until it is evident from tests made with an indicator, or simply by the degree of "bite" on the tongue, that only a very slight excess of lye remains Since alkali will largely remain in the aqueous phase when the soap is subsequently grained out, and must be neutralized in later processing of the spent lye to recover the glycerol, a large excess is avoided The actual alkali content of the spent lye will not usually be greater than about 0 3%, in terms of sodium carbonate Excessive addition of water at this stage increases the cost of glycerol recovery, although the solution must be kept sufficiently dilute to insure proper graining out The proper consistency of the batch is judged by the operator from the appearance of samples withdrawn in a ladle or on a trowel

The soap is grained out by the addition of saturated or nearly saturated brine (sodium chloride) solution while boiling is maintained Addition of the brine is controlled by observing the appearance of samples withdrawn as before After the graining operation is completed, the steam is shut off, and after settling overnight, the spent lye is withdrawn from the soap curd

The second change is carried out by adding water and boiling the soap until it is again completely liquid, or "closed" Additional fat and lye are then added to the kettle, and the operations of saponification, graining, and settling are repeated as before In some cases, the entire cycle of operations is repeated a third time

Saponification in the manner outlined above will not complete the reaction of the last small portions of fat in the charge, hence a final "strong" change is necessary, in which the charge is boiled and grained out with an excess of lye, rather than with salt The "half spent" lye resulting from

[7] E G Thomssen and C R Kemp, *Modern Soapmaking* MacNair Dorland Co , New York, 1937

this operation is not processed for glycerol recovery, but is used to saponify additional charges of fat

After the strong change the charge may be finished, although if a slight excess of alkali in the finished soap is less desirable than a slight excess of salt, another brine change will be interposed between the strong change and the finish

In finishing the batch, the soap is closed as before, by boiling with water, and the addition of water and lye is so controlled as to bring the system to the proper composition to permit the soap to separate into neat soap and a niger of suitable volume The proper condition for this separation is again judged from the appearance of the batch, as indicated above, this stage of the process calls for extreme skill on the part of the soapmaker After a further period of settling, the neat soap is drawn off from above the niger, and pumped to other parts of the plant for incorporation into various finished soap products The niger is diverted to lower grade products by reboiling, salting out, etc The entire soap boiling process consumes from 4 to 10 days

In a variation of the above process, the soap is finished in a grained condition, rather than as neat soap, by the addition of brine after the strong change Such a product contains less water than neat soap, hence a relatively hard soap can be made from vegetable oil foots, low titer greases, or other cheap materials This variety of soap is known as curd soap

In the manufacture of yellow laundry soaps, or other soaps containing rosin, the rosin is either saponified separately, or added after the glycerol has been removed by the first brine changes Rosin of course contributes no glycerol to the spent lyes, and it is considered to "hold up" glycerol, if present in the first stages of saponification

Soap is often bleached during the boiling operation by the addition of sodium hypochlorite solution, or other bleaching agent, directly to the kettle

(c) *Soaps by the Semiboiled and Cold Processes*

In the semiboiled and cold processes there is no graining out or separation of the soap into neat and niger phases The fat is simply caused to react with a quantity of alkali solution corresponding very closely to that actually required for saponification, and all of the glycerol produced is retained in the finished soap

Both semiboiled and cold made soaps are prepared in relatively small batches in crutchers, or cylindrical round bottom tanks equipped with steam jackets and a special mixer designed for handling stiff materials If the batch is to be semiboiled, the fat and strong lye are run together and mixed and heated somewhat short of the boiling point until saponification is substantially complete, the proportions of fat and lye being adjusted until

the final alkalinity of the batch amounts to no more than a small fraction of 1% in terms of free sodium hydroxide Potash or soft soaps are commonly made by the semiboiled process

In the cold process, mixing is carried out at substantially room temperature so that little more than thorough emulsification occurs in the crutcher Very strong lyes, 35–45° Bé, are employed the emulsion of strong lye and fat formed in cold saponification is said to be of the water in oil type[a] as distinguished from the oil in water type produced in soap boiling Saponification is completed after the soap is run into frames several days at a reasonably warm atmospheric temperature being required for completion of the process

Since there is no opportunity in the manufacture of cold made soaps to adjust the proportions of fat and lye according to the reaction of the two the charge must be quite carefully calculated However, these soaps quite commonly contain a substantial excess of either alkali or fat Any addition of builders, perfumes, or coloring material to cold made or semiboiled soaps must of course take place in the crutcher

Semiboiled and cold made soaps are frequently prepared from fatty acids, as well as from fats

(d) *Continuous Saponification Processes*

In order to avoid the excessive waste of heat and time consumed in the conventional soap boiling process, a number of continuous saponification processes have been devised, and at least two of these are now in large scale commercial operation The greatest utility of the continuous processes would at present appear to be in the manufacture of spray dried granules or beads Since the washing effect of ordinary soap boiling is not obtained in continuous saponification, this process would appear to be less suitable for the manufacture of high grade toilet soaps

The continuous soapmaking process of Mills involves successive steps of fat splitting[8] and saponification,[9] which are illustrated in the diagrams of Figures 93a and 93b In these diagrams, *1* and *2* are deaerators through which the water and fat are passed to effect a thorough removal of dissolved oxygen High pressure pumps, *3* and *4* draw the water and fat in controlled proportions through the meters *5* and *6*, and force it into the heaters *7* and *8*, which are connected to the heating unit *9* The latter may be a Dowtherm vaporizer or other suitable heating device In the heaters the water and fat are raised to the operating temperature, which is between 365° and 600°F, and preferably about 470°F It is of course necessary for the pumps to raise the pressure on both water and fat to that

[8] V Mills (to Procter & Gamble Co), U S Pat 2 156 863 (1939)
[9] V Mills (to Procter & Gamble Co), U S Pat 2 159 397 (1939)

FIG 93a —Mills continuous soapmaking process (fat splitting) [8]

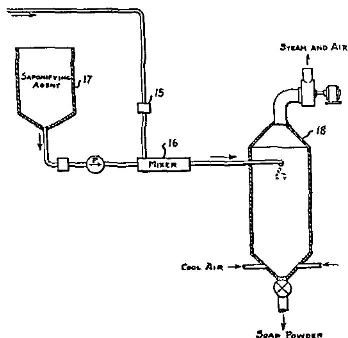


FIG. 93b —Mills continuous soapmaking process (saponification).[8]

corresponding to the pressure of saturated steam at this temperature, or to 150 to 1600 pounds per square inch

Beyond the heater, a proportioned amount of catalyst for the fat splitting reaction is introduced into the fat stream from tank *10*, by pump *11* The catalyst consists of zinc oxide, or other suitable material The heated water and fat are introduced at the top and bottom, respectively, of the tower or autoclave *12*, and splitting of the fat takes place as the water and fat move in countercurrent contact through the tower A tower 2 feet, 6 inches in diameter, and 50 feet high, is said to have a capacity of 7500 pounds of tallow per hour and to produce a 98–99% splitting of the fat at 470°F and 600 pounds pressure, the fatty material remaining in the tower for about one hour The tower, like the other portions of the apparatus which come into contact with hot fatty acids, is made of Type 316 or other suitable corrosion resistant alloy The internal construction of the tower is not specified

The glycerol produced by hydrolysis of the fat collects in the bottom of the tower, in the form of "sweet water" containing about 24% glycerol As it is released from pressure in flash chamber *13*, sufficient water is evaporated to increase the glycerol concentration to about 32% Fatty acids from the top of the tower are released through automatic pressure control valve *14*, and are passed through meter *15* to mixer *16* Although the acids dissolve about 11% of water at the operating temperature, this water is said to contain no more than about 0 1% glycerol

In the mixer, saponification is effected by bringing the fatty acids into contact with a metered stream of caustic soda or soda ash solution, supplied from tank *17* The admixture of unheated alkali decreases the temperature in the mixture somewhat below that at which the fatty acids leave the tower The hot soap discharges into spray chamber *18*, where it is converted in the usual manner into a granular product of 15–25% moisture content

Another continuous soapmaking process,[10] in which neutral fat is saponified and glycerol is recovered from the soap by volatilization, is illustrated diagramatically in Figure 94 Fat and strong caustic soda solution are withdrawn from tanks *1* and *2* by high pressure pumps, heated in preheaters (which are not shown) to about 275° and 180°F, respectively, mixed in the jet type mixer, *3*, and reacted to form soap during passage of the mixture through a series of heating coils represented at *4* The soap is discharged at about 550°F into the evacuated chamber, *5* where water and glycerol are flashed off, and the latter is recovered in the con

[10] See various U S Pats of B Clayton B H Thurman *et al* (to Refining Inc) including the following—(A) 1 968 526 (1934) 2 019 775 (1935) (B) 2 037 006 (1936) 2 123 647 (1938), and (C) 2 283 776 (1942), and also M Mattikow, *Oil & Soap* **17**, 184–188 (1940)

denser system shown at *6* The flash chamber is provided with an agitator of the sweep type, which is not shown Vacuum is maintained on the system by steam-jet ejectors and barometric condensers, as shown at *7*, *8*, and *9*

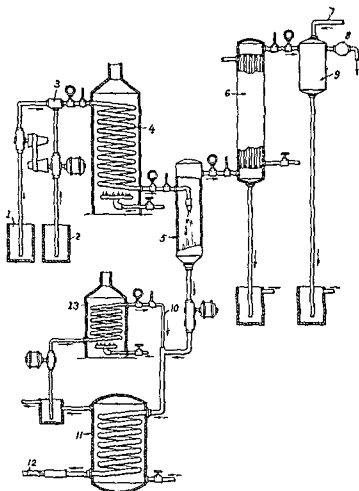


FIG 94—Clayton continuous soapmaking process [10c]

The soap, almost anhydrous, and with its glycerol content reduced to 0 5–1 0%, is taken from the flash chamber by water cooled screw conveyors, and after rehydration to any desired degree by steam injected at *10*, is further cooled, as at *11*, to about 200°F, and then extruded from a plodder, in a form suitable for milling, at *12* Steam generating equipment is represented at *13* The conveyors between the flash chamber and the plodder are designed to compact the cooled soap mass, and thus form a plug, which enables a vacuum of about 29 inches to be continuously maintained on the flash chamber A reaction time of but 5 minutes is said to be required for complete saponification of the fat

In the above process, a factor to be considered is the possible loss of glycerol through decomposition at the high operating temperatures employed The rate of destruction of glycerol in contact with alkalies at high temperatures is the subject of a recent communication by Mattikow and Cohen [11]

(e) *Recovery of Glycerol*

The recovery of glycerol from spent lyes is an important operation in any soap plant, as glycerol is an important by product of soapmaking

The spent lyes contain, in addition to about 5–15% glycerol, a considerable and variable quantity of salt, a small amount of free caustic soda, traces of dissolved soap, and certain organic impurities derived from the fat The first step in glycerol recovery is treatment of the lye with aluminum sulfate and sulfuric or hydrochloric acid The addition of about 4 to 14 pounds of aluminum sulfate to each 1000 pounds of lye precipitates any dissolved soap in the form of insoluble aluminum salts, and reacts with the excess caustic soda to form a flocculent precipitate of aluminum hydroxide which has a high adsorptive capacity for albuminous material or other organic impurities Sufficient acid is also added to neutralize any caustic soda remaining after reaction with the aluminum sulfate After treatment is completed the clarified lye is filtered in ordinary filter presses

The treated lye is evaporated to precipitate the bulk of the salt, and concentrate the solution to so called 80% crude glycerine Vertical tube double effect evaporators are commonly used for evaporating the solution to a glycerol concentration of about 40%, at which point it is known as "half crude" glycerine Separation of the bulk of the salt occurs in the second effect, the salt settling to the bottom of the evaporator and thence falling into salt drums Valves are placed in the pipes leading from the evaporators to the salt drums, so that the latter may be periodically cut off from the evaporator proper, and emptied The recovered salt, after washing and drying, is reused for salting out new batches of soap

In the further concentration of half crude to 80% crude glycerine, the first effect is cut out of the system, or a separate single effect evaporator is used, high pressure steam being employed in either case for heating the solution With the usual vacuum of 26 to 28 inches on the evaporator, a concentration of 80% will be reached when the temperature has risen to about 190° to 200°F , excessive losses of glycerine will occur if further concentration is attempted

Ordinary 80% crude glycerine contains a considerable amount of salt, and various other impurities, both organic and inorganic Purification and further concentration of this product, to yield the commercial grades of C P glycerine, U S P glycerine, dynamite glycerine, etc , is carried out

[11] M Mattikow and B Cohen, *Oil & Soap*, **20**, 135–136 (1943)

by fractionally distilling the glycerol from the nonvolatile impurities under vacuum, with the aid of superheated steam, and treating the distilled product with bleaching carbon and various chemicals

2. Solidification and Drying of the Liquid Soap

(a) *Framing and Drying of Framed Soaps*

The simplest method of converting neat soap, or other hot liquid soap to a solid form suitable for forming into bars, is known as framing This consists simply of running the liquid soap into frames and allowing it to solidify spontaneously in the form of large cakes Various coolers have been devised in which the soap is quickly solidified in small, water cooled frames, but these do not appear to have attained wide use, at least in the United States

The frames consist of a bottom, mounted on wheels, and four removable sides, which can be clamped together to form a liquidtight compartment, and yet be readily removed from the solidified cake A frame of soap usually weighs 1000 to 1200 pounds, and is shaped in the form of a high, narrow rectangle, for maximum convenience and economy in subsequent cutting operations About 3 to 5 days are ordinarily required for the solidification of neat soap, cold made soaps may require slightly longer, since saponification is completed in the frames

The frames of soap are cut into slabs and then into cakes by being forced through metal frames set with thin taut wires The cakes or blanks resulting from this operation must be dried to some extent before they can be stamped and wrapped Drying is carried out by passing the blanks through drying rooms or tunnels, where they are subjected to the action of warm, dry, circulating air Drying occurs largely on the surface, hence the moisture content of the whole bar is not usually reduced by more than 3% to 5%

Floating soaps produced by framing simply contain a considerable proportion of air beaten into the soap mass in the crutcher This air is in the form of very fine, almost invisible bubbles, which are readily retained by the viscous soap entering the frames

Added materials, such as builders, antioxidants or stabilizers, perfumes, etc , are crutched into the kettle soap before framing

(b) *Manufacture of Soap Chips*

Soap chips are manufactured not only to be packaged as such, but also to be milled and plodded into toilet soap bars, the solidification and drying of soap in the form of chips having in modern plants entirely supplanted other methods of preparing neat soap for milling

Solidification of soap for the production of chips is accomplished on a

chilling roll, about 4 to 5 feet in diameter, and twice to three times as long, cooled internally by the circulation of water The molten soap, which may be pure neat soap if the chips are to be milled, or a mixture of neat soap and builders if they are to be packaged for home laundry use, is picked up or discharged onto the surface of the roll, where it is spread into a thin and uniform layer by the action of a smaller feed roll set above the chill roll, with only a slight clearance between the two The soap, solidifying as the roll slowly revolves, is marked off into narrow ribbons by a series of needle points bearing against the roll surface, and is thereafter removed from the roll by a scraper blade

The soap ribbons fall from the chill roll onto a wire mesh conveyor, which carries them slowly back and forth through a tunnel dryer heated by steam coils and provided with forced circulation of air By regulating the temperature within the dryer, and the speed with which the conveyor operates, the moisture content of the material may be quite accurately controlled, about 13–14% moisture being desired in a product which is to be milled The ribbons taken from the chilling roll naturally break up into chips in subsequent handling, after they have dried sufficiently to become brittle Care is exercised in drying to avoid heating the chips enough to cause them to partially melt and stick together or adhere to the conveyors

Chips taken hot from the dryer cannot be packaged or stored directly, hence the final stage of the drying operation consists of circulating cool air through the material to reduce its temperature

(c) *Spray Drying*

Spray drying has very largely supplanted older comminution processes for the production of soaps in a finely divided, quickly dissolving form It is used for the preparation of both pure soap products and those which include moderate proportions of builders

This process consists, in the simplest terms, of forcing the molten soap through spray nozzles in the top of tall towers, the small particles thrown out by the nozzles becoming solidified and drying as they fall through a parallel or countercurrent stream of heated air

The process is subject to many variations having to do with the temperature and composition of the liquid soap, the temperature and pressure existing within the tower, and the mechanical devices used for forming the spray, all of which have their effect on the characteristics of the finished product However, data on the actual operation of the different processes are not generally available

Spray-dried soap products have become very popular in recent years, and have to a considerable extent replaced soap chips and bars for general household use The object in preparing a spray dried product for household use

is to obtain a material which is composed of very thin and easily dissolved particles

The properties of a good spray-dried household soap are somewhat critical It is essential that the soap be easily dissolved, therefore the individual particles must be very thin and uniformly dried On the other hand, they should not be so finely divided as to be dusty A large bulk in the package is desired, hence the particles are preferably porous and cellular in nature A particularly effective spray drying process is that of Lamont,[12] which produces soap particles in the form of hollow, thin walled spheres, or beads

(d) Continuous Solidification of Bar Soaps

A patent issued to Mills[13] discloses a method for the continuous solidification of a bar soap This method is now used on a large scale for the manufacture of a popular floating soap, having replaced the framing process formerly used

The apparatus used in the Mills continuous process is illustrated in Figure 95 The molten neat soap contained in tank *1* is forced by high pressure pump *2* to heater *3*, where its temperature is raised to about 390°F The heated soap, at a corresponding pressure of about 250 pounds, is sprayed into flash chamber *4*, where sufficient water is removed through condenser *5* to reduce its moisture content to about 20% The hot soap reaching the bottom of the flash chamber, still in the neat phase, is forced by pump *6* into the continuous crutcher or mixer, *7* In this mixer, perfuming materials are incorporated, and sufficient air is whipped into the soap mass to reduce the specific gravity of the finished bar to about 0 8 A pressure of 10 to 20 pounds per square inch is maintained on that part of the system forward of the pump

The cooling and agitating device indicated at *8*, is a special form of Votator, not unlike that used for the solidification of shortenings, lard, and margarine, but cooled by the circulation of cold water The aerated soap, entering the Votator at about 220°F , is rapidly cooled, revolving scraper blades within the cooling chamber maintaining a high rate of heat transfer between the soap and the chamber walls Beyond the cooling chamber there is a mixing chamber in which the cooled soap is thoroughly agitated by revolving paddles intermeshing with stationary baffles Finally, the soap is extruded through orifice *9* onto conveyor belt *10* in the form of a continuous slab, which is divided into cakes by cutter *11* The temperature at which the slab is extruded, which is critical, is generally between

[12] D R Lamont (to Industrial Spray Drying Corp), Brit Pat 291 041 and U S Pat 1 652 900 (1927)

[13] V Mills (to Procter & Gamble Co) U S Pat 2 295 594 (1942)

about 140° and 160°F The cakes are further cooled to about 100°F, and are then continuously stamped into the finished soap bars

Although the process is novel in accomplishing the continuous formation of finished soap bars of relatively low moisture content from neat soap, it is not only in this accomplishment that its usefulness resides One of the principal objects of the process is to produce a soap which is largely in the easily dissolved beta phase peculiar to milled soaps, rather than in the less easily dissolved omega phase of framed soaps (see page 335) The essential

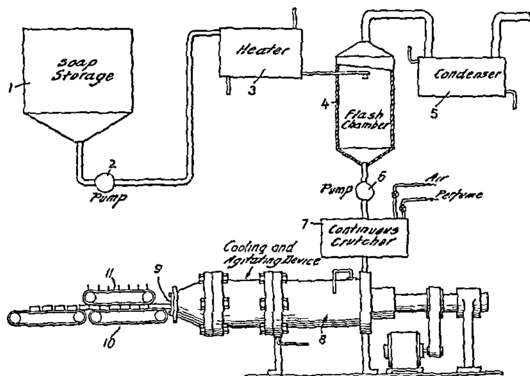


FIG 95 —Mills continuous process for the solidification of floating soap bars [14]

condition for formation of the beta phase is agitation of the soap mass at a temperature and moisture content at which this phase is the stable form The critical temperature below which the beta rather than the omega form is stable varies for different soap formulas, however for a 20% coconut oil–80% tallow soap containing 20% moisture, it is said to be in the neighborhood of 160°F Preliminary reduction of the moisture content of the neat soap from about 30% to about 20% is an important feature of the process, since increase in the moisture content lowers the critical temperature

The Mills process is claimed to be applicable also to the manufacture of soap flakes[14] and spray dried soap,[15] in which the soap is largely in the

[14] V Mills (to Procter & Gamble Co), U S Pat 2 295,596 (1942)
[15] V Mills (to Procter & Gamble Co), U S Pat 2,295,595 (1942)

beta phase If the soap is taken from the Votator at a temperature slightly below the most suitable temperature for the extrusion of bar soap, it is said to be softer in consistency than if processed at a higher temperature, and hence is in a suitable form for spraying or forming into chips or flakes Presumably some difficulty might be experienced in drying the chips or spray at a temperature low enough to avoid reversion to the omega phase

Another method for producing a floating soap of low moisture content and high solubility is disclosed by Bodman [16] This method involves heating pellets from the plodder in a special steam jacketed mixer until the soap mass is plastic and homogeneous, aerating the plastic mass, and then forming the latter into bars It is claimed that a desirable product is obtained from a soapstock containing less than 25% moisture, by heating to 160°

3 Mechanical Working of the Solidified Soap

(a) *Manufacture of Milled Soap Bars*

High grade toilet soap bars are almost invariably milled Milling and plodding of partially dried soap chips into bars accomplishes several objects which cannot be attained by simply allowing neat soap to solidify in frames By this process the moisture content of the soap may be reduced to less than 15%, whereas that of framed soap will hardly be less than about 30% The working undergone in the rolls produces a certain degree of orientation of the crystalline soap fibers, which contributes to the distinctive physical properties of the product Also this working converts the soap largely to the beta phase, as contrasted with the omega phase principally existing in framed soaps The milling process permits the addition of perfumes after the soap has become cold, hence perfumes may be used which are unstable in the presence of hot alkalies or are relatively volatile

The recommended moisture content of chips which are to be milled is between about 13% and 14% Chips of much lower moisture content are difficult to mill properly, whereas those of high moisture content are too gummy and soft to mill well or to handle well in the plodders, cutters, and presses

The first operation in the manufacture of milled soaps consists of mixing weighed batches of chips in amalgamators, or heavy horizontal mixers, with perfume, dyes, titanium dioxide, or other whitening material, etc From the amalgamator the mixture is transferred to the mills These consist of a series of rolls through which the soap mass is passed in the form of a thin sheet The individual rolls rotate at different speeds, so that the sheet, in passing between adjacent rolls, is not only compressed, but also

[16] J W Bodman (to Lever Bros Co), U S Pat 2,215,539 (1940)

subjected to an intensive shearing action The soap is stripped from the last roll in the form of thin ribbons, as in the preparation of soap chips

Milling rolls were formerly made only of stone, granite being the preferred material for their construction, but now they are commonly made of chilled iron Iron rolls are made in hollow form, and cooled by circulating water, which carries away the frictional heat generated in the soap during milling Hence they may be run at a higher capacity than granite rolls, without danger of overheating the soap

Compression of the milled soap into a dense, coherent form, suitable for forming into bars, is accomplished in a plodder This machine is not unlike an ordinary sausage grinder It consists of a hopper communicating with a horizontal chamber of circular cross section, in which revolves a spiral compression screw The soap mass is forced through a compression cylinder containing a plate with multiple perforations, and then extruded under high pressure through an orifice in the end or "nose" of the device in the form of a continuous bar The compression cylinder is jacketed for the circulation of cooling water, and the nose is electrically heated Passage of the bar of soap through the heated nose melts the surface just sufficiently to impart to it a high polish

The extruded bar emerges to a cutting table where it is cut into blanks by a wire cutter The blanks are stamped into finished soap bars in automatic presses fitted with dies bearing the lettering or design desired, and are then automatically wrapped

There are certain variations of the above described process A preplodder is often placed between the milling rolls and the plodder The preplodder is similar to the plodder except that the nose is omitted, hence it extrudes the soap in the form of small round rods, which are cut into pellets by a revolving cutter Feeding of the plodder is facilitated by thus preforming the feed material It is also possible to eliminate the milling rolls entirely by passing the soap through a succession of suitably designed preplodders equipped with orifice plates with small perforations Forcing of the soap through these small openings under high pressure provides a shearing action which accomplishes the same purpose as milling The patent issued to Bodman[17] describes a homogenizing device of this type, in which very minute orifices (comparable to those in 20- to 40 mesh screens) are employed, and the soap mass is maintained in a plastic condition during the operation by the application of heat through jackets surrounding the compression cylinders

(b) *Manufacture of Milled or Polished Flakes*

Milled flakes are made only from pure soap, with no builder added, and are the highest grade and most expensive form of the various quick dis

[17] J W Bodman (to Lever Bros Co) U S Pat 2 005 333 (1935)

solving soap products They are produced by repeatedly milling dried chips of relatively low moisture content (about 10–11%) through special, close-set, water-cooled steel rolls Drying of these flakes to a brittle form is actually accomplished on the rolls, and the flakes are ready for packag ng after milling is completed A very thin flake is produced, which has a distinctive polished appearance and the quick-dissolving characteristics of milled soap in the bar form.

(c) Preparation of Powdered Soaps

The mechanical reduction of soaps to powdered form is relatively little practiced since the advent of spray-drying processes, although it is still necessary to grind soap powders for special purposes, particularly for the manufacture of shaving powders, dentifrices, and certain other toilet goods

It is necessary to dry soap chips to a very low moisture content, i e, below about 3%, in order for them to be sufficiently pulverulent to grind well Chips of this low moisture content will under most atmospheric conditions absorb moisture from the air, hence the dried chips must be imme diately ground, or stored without free access to the air The chips ground for toilet purposes consist only of very pure soap made by the full boiled process

Reduction of the dried chips is carried out in attrition mills, which are equipped with air separators to separate the finer particles and recycle coarser particles to the feed An open circuit with a constant throughput of cooling air is recommended, to avoid overheating the powder Some degree of drying is also accomplished in an open circuit, the finished powder often containing as high as 99% of anhydrous soap

FRACTIONATION OF FATS AND FATTY ACIDS

1. Introduction

Oils, fats, or mixed fatty acids are fractionated in order to provide new materials more useful than the old. Often fractionation is carried out merely to rid a fatty material of minor quantities of an unwanted component. Such is the fractionation sought in the winterization of vegetable oils or fish oils. However, separation of fat or fatty acids into fractions will often provide two or more improved products from the same original material. Thus, for example, the pressing of tallow fatty acids yields commercial oleic and stearic acids, each of which have properties which render it more suitable for specific purposes than the mixed acids.

Although the fractionation processes in use at present consist principally of those which have been in operation for many years, some methods have been but lately introduced, and there is every prospect that fractionation may generally assume greatly increased importance in the future. In order to appreciate the potential utility of fractionation techniques it is necessary to recall that in very few cases can present oil and fat products be said to have completely satisfactory compositions. Lard, shortenings, and margarine, for example, would possess much greater stability and in consequence probably be better edible products if they contained no acids more unsaturated than oleic acid. On the other hand, most paint and varnish oils would be improved if they contained more of the highly unsaturated compounds which are undesirable in edible products, and lesser quantities of more saturated components. Soaps invariably contain fatty acids which could be eliminated to the improvement of their quality.

In some cases natural fats contain such a variety of fatty acids that this variety in itself constitutes a disadvantage. An excellent example of such unfortunate variety in fatty acid components is furnished by sardine oil and other fish oils. These oils contain large proportions of very highly unsaturated fatty acids, but also quite substantial amounts of completely saturated acids. The completely saturated acids prevent fish oils from being entirely satisfactory drying oils, and on the other hand, the highly unsaturated acids make them relatively poor materials for the manufacture of edible products. It is not feasible at present to convert fish oil into fractions consisting respectively of glycerides of saturated and monoethenoid acids, and glycerides of fatty acids with two or more double bonds, but if

this could be done, the former would be entirely suitable for use in high grade food products and the latter would constitute an excellent drying oil

The ultimate in fractionation has been outlined in a somewhat fanciful but illuminating article by Potts[1] It would simply involve splitting the available oil and fat supply into glycerol and fatty acids, separating the latter into fractions comprising the individual acids or classes of acids, and then diverting the latter to food, paint, soap, etc, according to their particular adaptabilities, either with or without previous re esterification with glycerol, as might be required Such a scheme for fat utilization is of course fantastic in its over all aspects, but it cannot be doubted that new "tailor made" fats, prepared according to the principles above outlined, will henceforth find increasing use

Fractionation can usefully be applied to both fats and fatty acids However, it is to be noted that in the case of fats, the degree to which the properties of the material may be modified is limited by the highly mixed nature of natural glycerides The glycerides tend to assume the average characteristics of the fatty acids, since three different acids of diverse nature and properties may be combined within a single triglyceride molecule If fractionation is carried out on the free fatty acids or their monoesters, the attainable separation is limited only by the efficiency of the fractionation methods, and with the use of sufficiently effective techniques might conceivably be carried to the point of near quantitative separation of the individual acid or esters

2 Fractional Crystallization

(a) *Winterization of Oils*

The process by which the higher melting glycerides are removed from oils is termed winterization, from the circumstance that separation was formerly carried out by simply allowing the oil to stand and settle out in outside tanks during the winter The present large demand for such oil makes it necessary to employ artificial cooling and filtration of the liquid from the solid portions

Practically all of the winterized vegetable oil at present manufactured consists of cottonseed oil Such oils as soybean, corn, sunflower, olive, and sesame oil do not require winterization to remain liquid at low temperatures (although corn and soy bean oils must be cleared of waxes to prevent clouding), and it is not feasible to winterize peanut oil because of its tendency to deposit difficultly filterable crystals Edible oils which will remain substantially liquid at temperatures of 40° to 45°F are in particular demand in the United States because of the widespread use in this country of mechanical household refrigerators operating at these temperatures

[1] R H Potts, *Oil & Soap*, **18**, 199–202 (1941)

The problem of winterized oil manufacture resolves itself principally into a matter of producing crystals of a form that can be separated from the uncrystallized oil This is a matter of some difficulty At the relatively low temperatures required for crystallization the oil is quite viscous, the reluctance of substances to deposit well formed crystals in viscous media is well known, particularly when the molecules forming the crystals are large, as they are in the case of triglycerides The oil must be cooled with extreme slowness in order to produce filterable crystals, and even under the most favorable circumstances the final separation of solids and liquid is difficult and incomplete Because of the slowness of the operation and the poor separations obtained, ordinary winterization is one of the least satisfactory of present oil processing methods

It is customary to conduct the entire winterization operation in refrigerated rooms, although the chilling tanks may be placed in a room at atmospheric temperature if they are closed and well insulated In some plants the chillers are built in a very narrow form (in some cases as little as 2 or 3 feet in width), to facilitate heat transfer from their interior, and refrigeration is applied through the cold air of the room It is more usual, however, to employ tanks of conventional shape and size, and equip them with cooling coils The direct expansion of a refrigerant in the coils can scarcely be depended upon to provide the gradual cooling requisite for proper crystal formation They are usually designed, therefore, for the circulation of cold brine It is more or less essential to have the refrigeration system so arranged that the temperature of the brine may be easily varied and positively controlled In order to avoid shock chilling of the oil next the coils, the temperature differential between the brine and the oil should never be large A differential varying from about 25°F when the oil is at 75°F, to about 10°F when the oil is at 45°F, is usually satisfactory The coils must be quite closely spaced in the tank, as mechanical agitation of the oil to bring it into contact with the coils cannot be permitted after crystals have begun to form

As stated previously, an absolutely essential feature of the process is a slow rate of chilling Even when the greatest care is exercised in chilling, filtration of the cold, viscous oil from the relatively nonrigid crystals is a difficult matter, and carelessness in forming the crystals may easily lead to complete failure of the operation

The following represents a typical sequence of operations in the preparation of a highly winterized cottonseed oil The oil is charged to the chillers at a temperature of 70° to 80°F It is then cooled to 55°F in 6 to 12 hours At about this temperature the first crystals will appear in an average oil The cooling rate is then reduced somewhat, and an additional 12 to 18 hours is allowed for the temperature to drop to about 45°F The rate of crystallization will then be sufficiently rapid to cause a slight rise in the

temperature of the oil, even though the refrigeration input is maintained at a constant level The temperature will rise usually 2° to 4°, and then drop as before When it has dropped to a point slightly below the previous minimum (e g, to 42°F) the cooling is discontinued, and the batch is held at this temperature for a considerable time The exact duration of this latter holding period will depend upon the degree of winterization desired There will be progressive crystallization for an extended time after cooling has ceased, and the degree of winterization attained will depend much more upon the length of the holding period than upon the actual holding temperature A holding period of 12 hours will generally insure a cold test (time required to cloud at 32°F) of upwards of 20 hours

Filtration of winterized oils is usually carried out in ordinary plate and frame or recessed plate filter presses In order to convey the crystallized oil to the presses with the least possible disturbance and disintegration of the crystals, the chilled mass is usually dropped by gravity from the chillers into small closed pressure tanks or "eggs," from which it is forced to the presses with compressed air Low speed rotary pumps of the positive displacement type are less commonly employed for the same purpose If the chillers are of the closed type, and built to withstand moderate internal pressure, the oil may of course be transferred by air pressure directly from chillers to presses

Considerable filtering capacity is required, as compared with ordinary filtering operations, the average rate of filtration in handling a complete batch may not exceed about 1 pound of oil per hour per square foot of filtering surface Filtration must be conducted at a low pressure (about 5 to 20 pounds gage), as the application of high pressure will compress the filter cake and render it quite impermeable to the passage of oil The time required for both crystallization and filtration of a batch will generally be 3 to 6 days, although some plants operate on an even longer cycle

After filtration is completed and after the filter cake is removed from the presses, the cloths of the latter must be heated to melt and remove the fat crystals clogging their pores before the next batch of oil is filtered This is a difficult operation because, in melting the crystals, it is very undesirable to heat the metal frames of the presses or the rooms in which the presses are contained. It is good practice to have canopies equipped with exhaust fans mounted over the presses so that the cloths can be heated with a hand-operated jet of hot air or steam, and the latter exhausted from the room

Cottonseed oil with an iodine value of 108 will yield about 65% to 75% winterized oil and 25% to 35% of cake There will be no great difference in the iodine values of the two fractions, the iodine value of the oil will be about 111 to 114, and that of the cake will be about 90 to 95 Since the cake is liquid or substantially liquid at ordinary temperatures, it cannot be

used as a stiffening agent in blended type shortenings, but must simply be substituted in shortenings for ordinary cottonseed oil

Crystallization inhibitors, such as are commonly added to low pour point lubricating oils, are not used in edible winterized oils, although lecithin as a crystallization inhibitor for the latter has been patented [2] In the author's experience lecithin is not so much effective in completely preventing crystal formation as in retarding the time required for an oil to become solid or semisolid A sample of winterized cottonseed oil which at 32°F became clouded in 10 hours, pasty in 32 hours, and solid in 48 hours, was observed after the addition of 0 05% soya lecithin to cloud in 15 hours and become pasty in 150 hours

Occasionally oils will be encountered which fail to crystallize normally in the winterization process, even though they may be of ordinary glyceride composition A peculiarity of this kind was observed, for example by Ronzone[3] in the case of Chinese cottonseed oil It seems probable that abnormal habits of crystallization in otherwise normal oils are usually due to the presence in the latter of natural crystal inhibitors

The standard cold test of the American Oil Chemists' Society requires that a winterized oil remain clear after 5 5 hours immersion in ice and water However, most winterized cottonseed oils will pass such a test for 8 to 16 hours, and oils with a cold test of 20 hours or more are not uncommon From a practical standpoint, the time required for an oil to cloud at 32°F is less important than the amount and character of the crystals which the oil will deposit after a more prolonged holding period at a low temperature Some manufacturers test their winterized oils by means of cloud and pour tests conducted by the A S T M method for lubricating oils The cloud and pour points of an oil bear a more or less inverse relation to the time required for it to cloud at a low temperature An oil with a cold test of 15 hours at 32°F, for example, will have cloud and pour points of about 24°F and 20°F, respectively Unwinterized cottonseed oil will usually become quite solid in 1 hour at 32°F, and will have respective cloud and pour points of about 36°F and 28°F

Soybean, corn, and linseed oils are often chilled and filtered to remove waxes which cause them to become cloudy at low temperatures However, these waxes are present in hardly more than traces, and their removal is a much less critical operation than true winterization The oils may be chilled quite rapidly and filtered with relative ease

Peanut oil has higher cloud and pour points than cottonseed oil (about 40°F and 34°F, respectively), but the virtual impossibility of winterizing this oil appears to arise from its tendency to form peculiarly gelatinous

[2] D P Grettie (to Industrial Patents Corp) U S Pat 2 050 528 (1936)

[3] P E Ronzone *Oil & Soap*, **13**, 165–167 (1936)

and nonfilterable crystals, even when chilled very slowly, rather than from its containing any excessive proportion of solid material

Fish oils intended for use in paints or other protective coatings are usually winterized to remove relatively saturated glycerides which interfere with the drying of the oils to hard, nontacky films Cod liver oil or other medicinal oils may be winterized simply for the sake of the appearance of the oil in cold weather

According to Behr,[4] a sardine oil winterized for use in paints or varnishes should have a clouding time at 32°F of not less than 14 hours This writer observed that it was necessary to remove approximately 30% of high melting material from sardine oil to produce oil with a cold test of 20 hours, the saturated acid content of the oil (by the Twitchell method) being decreased from 22% to 17% in the process Further winterization, to increase the cold test of the oil to 90–100 hours, reduced the saturated acid content only to 16 75% Another lot of winterized sardine oil with an iodine value of 203 5 and a cold test of 40 hours was found to contain 17 5% of saturated acid Winterization of the oil not only caused it to polymerize more rapidly in the operation of heat bodying, but also made it more reactive with phenolic resins

Brocklesby[5] reported that in a laboratory experiment a temperature of 34°F was required to remove 21 8% of high melting glycerides from pilchard oil, the saturated fatty acid content of the oil being reduced to 17 0% However, in the winterization of fish oils, as in that of cottonseed oil, it would appear that the degree of winterization obtained should depend more upon the holding time at the minimum temperature than the actual temperature employed In another experiment Brocklesby found that various pilchard and sardine oils deposited from 17–32% of solid glycerides during a 24-hour holding period at 48°F

The equipment and technique employed in winterizing fish oils are not essentially different from those described above in connection with the winterization of cottonseed oil, although in the case of fish oils there is a somewhat more clean cut fractionation of the oil on the basis of the iodine values of the fractions, and somewhat more rigid and easily filterable crystals are obtained

(b) *Fractional Crystallization of Animal Fats*

The fractional crystallization of oleo stock (beef fat) to produce oleo oil and oleostearine is very old in the packing industry The process has changed very little since its inception and is carried out as follows

Crystallization of the fat, known in the industry as "graining" or "seed-

[4] O M Behr, *Ind Eng Chem*, 28, 299–301 (1936)

[5] H N Brocklesby, *The Chemistry and Technology of Marine Animal Oils* Bull No 59 Fisheries Research Board of Canada, Ottawa, 1941.

ing," is carried out in small rectangular tanks, holding about 600 pounds each, which are mounted on trucks After the tanks are filled with the melted fat, they are held for several days in a room maintained at approximately 90°F, during which time the crystals are formed As in other fractional crystallization procedures, it is essential that the crystals be formed slowly, in order that they will be large and easily separated from the uncrystallized oil

After the desired degree of crystallization has taken place, the trucks are transferred to another room, where the oleo stock, now in the form of a thick, pasty, and grainy mass, is scooped from the trucks by hand, and wrapped, in portions of a few pounds each, in canvas press cloths The latter are stacked in presses of the plate type, and subjected to moderate pressure, to yield oleo oil and residual cakes of oleostearine

The fractional crystallization and pressing of lard, to yield edible lard oil, and of grease, for the production of inedible lard oil, is similar to that of oleo stock, except that it is carried out at a somewhat lower temperature

(c) *Preparation of Commercial Oleic and Stearic Acids*

The stock used in the preparation of commercial stearic acid and oleic acid (red oil) usually consists of relatively low grade inedible tallow After the fat is split (usually by the Twitchell process) and the resulting fatty acids distilled, the latter are charged into small shallow pans and caused to solidify by being slowly brought to a temperature of about 40°F in a refrigerated room The solid cakes produced by this operation are individually wrapped in press cloths and subjected to moderate pressure in a hydraulic plate press, the expressed liquid acids constitute commercial oleic acid or red oil The latter is a rather impure product, in addition to oleic acid, it contains a considerable proportion of dissolved saturated acids, as well as the linoleic acid present in the tallow The residual solid acids constitute "single pressed" stearic acid

Press cakes from the cold pressing operation are recast into cakes and then subjected to a hot pressing, in a steam or hot water heated press of special design to yield "double pressed" stearic acid The residue from the hot pressing is recast and repressed at a slightly higher temperature to produce "triple pressed" stearic acid

Commercial stearic acid, as above prepared, actually consists of about 45 parts of stearic acid to 55 parts of palmitic acid with a minor quantity of oleic acid [6] The percentage of oleic acid will depend upon the temperature at which pressing is carried out, the pressure at which the press is operated, and whether the soft edges of the press cake are trimmed away and recycled

[6] B Nicolet, *J Ind Eng Chem* 12, 677-679 (1920)

Different lots and grades of stearic acid will contain 1–10% oleic acid, and have titers of about 53–55.5°C. (see page 434)

(d) *Fractional Crystallization from Solvents*

Fractional crystallization of fats from solvents, if practiced commercially at all, is carried out on but a very limited scale. However, there is reason to believe that this method of fractionation may attain importance in the future. A similar process is extensively used in the petroleum industry, for the dewaxing of lubricating oils.

The use of a solvent in fractional crystallization is advantageous in a number of respects. The admixture of even a small proportion of solvent with an oil very markedly lowers the viscosity of the latter (see page 55). Lowering the viscosity of the medium in which crystallization occurs facilitates the orientation of molecules, and permits well formed crystals to be deposited with relative rapidity. Thus the use of a solvent avoids the necessity of employing very long crystallization times to obtain large, well formed, and filterable crystals. After the crystals are formed, separation of the residual oil-solvent mixture from the crystals is effected much more readily and more cleanly than is possible in the case of oil alone. Furthermore, the solvent dilutes the oil entrained with the crystals in the filter cake, and thus reduces the entrainment of oil. In most cases it is feasible to wash the cake with fresh solvent, thereby rendering entrainment negligible.

One of the greatest potential advantages of solvent crystallization is the elimination of excessive hand labor in the fractionation of fatty materials containing large proportions of solids, such as lard, tallows, greases, or mixed tallow fatty acids. Mixtures of these materials with solvents are sufficiently fluid to be handled and separated mechanically, and would not require the excessive labor involved in crystallizing and pressing these materials by present methods.

A recent series of publications by Bailey and co-workers[7, 8] has indicated the feasibility of employing fractional solvent crystallization not only to facilitate present fractionation processes, but also to prepare useful new products. In one series of experiments,[7] ordinary refined cottonseed oil with an iodine value of 107.6 was winterized with an equal weight of petroleum naphtha (Skellysolve B), the minimum temperature employed being 2°F. Without washing the filter cake, a yield of 77.1% of winterized oil was obtained, which had a cold test of over 72 hours, and cloud and pour points of 20°F., and 18°F., respectively. Winterization of peanut oil (iodine value 97.7) with the same solvent in the ratio of 3 parts of solvent

[7] A. E. Bailey, R. O. Feuge, E. A. Kraemer, and S. T. Bauer, *Oil & Soap*, 20, 129–132 (1943).

[8] E. A. Kraemer, B. A. Smith, and A. E. Bailey, *Oil & Soap* 20, 235–240 (1943).

to 2 of oil, at 5°F, produced in a yield of 80 1% an oil with a cold test of 26 hours and cloud and pour points of 28°F and 26°F

By hydrogenating peanut oil to an iodine value of 70 2, and fractionally crystallizing the hydrogenated oil from three times its own weight of petroleum naphtha at 3°F, 78 1% of a liquid oil was obtained with the following characteristics iodine value, 75 8, cloud point, 36°F, pour point, 28°F, keeping quality by the Swift accelerated test, 35 hours This oil was notable for being liquid at ordinary temperatures and yet having a very low iodine value and a high degree of resistance to oxidation or gum formation It was suggested as a substitute for olive oil, as a textile lubricant, and as a suitable ingredient of cosmetics and fine lubricants

In a further series of experiments,[8] a hard butter somewhat similar to cocoa butter in its low melting point and short plastic range was prepared from cottonseed oil by hydrogenating the latter to an iodine value of approximately 25 and crystallizing high melting glycerides therefrom until a residue was left comprising 27 9% of the original oil Four parts by weight of solvent (petroleum naphtha) were used to each part of oil, and the minimum temperature of crystallization was 35°F

Low-titer oils having titers below 0°C, which are suitable for sulfonation and other purposes, are readily prepared by fractionally crystallizing the mixed fatty acids of cottonseed or peanut oil from solvents at temperatures in the range of 5° to 25°F and re esterifying the liquid acid fraction with glycerol

In considering the solvent fractional crystallization of fats, and in fact all fractionations of fatty materials, it is necessary to emphasize that it is by no means necessary for fractionation to closely approach quantitative separation of the different individual glycerides or fatty acids for it to be highly useful Often even a very crude separation will so profoundly affect the characteristics of a material as to fit it to entirely new uses In many cases very precise fractionation is neither necessary nor desirable

In the case of the fatty acids, the separations attainable by fractional crystallization are in some cases limited by the tendency of the acids to form mixed crystals and soluble compounds (see page 70) Thus Smith[9] found that oleic acid formed a eutectic with palmitic acid containing about 94% oleic and 6% palmitic acid, and a eutectic with stearic acid containing about 98% oleic acid and 2% stearic acid Stewart and Wheeler[10] found in the system oleic–linoleic acid a eutectic at about 75% linoleic acid, and in the system oleic–linolenic acid a eutectic at 83–85% linolenic acid No eutectic was observed in mixtures of linoleic and linolenic acids

Singleton and Bailey[11] have shown that tocopherol concentrates com

[9] J C Smith *J Chem Soc*, **1939**, 976–980

[10] H W Stewart and D H Wheeler, *Oil & Soap*, **18**, 69–71 (1941)

[11] W S Singleton and A E Bailey, *Oil & Soap*, **21**, 224–226 (1944)

parable to those obtained by molecular distillation can be obtained from vegetable oils by almost completely removing the glycerides by fractional crystallization from solvents at low temperatures Partially hydrogenated cottonseed oil, with an iodine value of 59 5, yielded a concentrate containing 32 1% tocopherols by crystallization of the oil from 8 times its own weight of acetone, at −74°C

3. Liquid–Liquid Extraction

(a) Theory

The efficacy of liquid–liquid extraction as a means of fractionating fatty mixtures is due to the circumstances that

(a) the affinity of polar organic solvents for fatty acids and their esters increases with increased unsaturation of the acids, whereas,

(b) the affinity of nonpolar solvents for these materials does not vary greatly according to their degree of unsaturation

As a practical consequence of the above, it will be found that when a polar solvent is brought into contact with an oil with which it is but partially miscible, and the two phases are allowed to come to equilibrium with each other and then separate, the portion of oil dissolved in the solvent will be more unsaturated than the portion remaining undissolved The following example, furnished by Freeman,[12] is illustrative One part by volume of soybean oil with an iodine value of 136 was agitated with four parts of furfural at a temperature of 27°C , and the two were allowed to separate By distilling the furfural from each fraction, there was obtained 28% of an extract with an iodine value of 146, and 72% of residual oil or raffinate with an iodine value of 132

As a further consequence of the principles set forth above, if an oil is similarly treated with two solvents, polar and nonpolar, which are each completely miscible with the oil, but relatively immiscible with each other, the portion of the oil dissolving in the polar solvent will be more unsaturated than that going into the nonpolar solvent Again an example given by Freeman[12] may be cited One part of mixed linseed oil fatty acids with an iodine value of 173 was treated at room temperature with one part of petroleum ether and two parts of furfural The portion of fatty acids recovered from the furfural had an iodine value of 193, while that recovered from the hydrocarbon had an iodine value of 166

While reference has been made above simply to polar solvents, actually, different polar solvents differ considerably in their effectiveness as agents for liquid liquid extraction, according to the number of polar groups in relation to the size of the molecule, and also their position in the molecule

[12] S E Freeman (to Pittsburgh Plate Glass Co), U S Pat 2 200,391 (1940)

According to the rule stated by Freeman,[12] for a solvent to be effective it must contain at least one polar group to each 4 to 6 carbon atoms in the molecule, and in the case of the weaker polar groups this ratio must be somewhat increased. The permissible number of carbon atoms for each of several groups is listed in Table 158.

Among the polar solvents which have been reported to be effective in liquid–liquid extraction are the following: nitroethane, methyl cellosolve, methyl formate, methyl levulinate, furfural, propionitrile, trimethyl phosphate, acetaldehyde, triethyl phosphate, acetonyl acetone, diacetyl, nitromethane, glycol diacetate, ethyl oxalate, methyl cellosolve acetate, methyl lactate, ethyl lactate, cellosolve, ethyl maleate, acetic anhydride, carbitol, etc. However, furfural appears to combine selective action towards unsaturated acids with other desirable characteristics to an optimum extent and so far as the author is aware, is the only polar solvent which has been used to any extent in practice. Furfural is miscible with fatty acids and their monoesters at ordinary temperatures, but is completely miscible with glycerides only at a somewhat elevated temperature. Hence, on the acids and monoesters it can be used only in connection with a non-

TABLE 158
PERMISSIBLE NUMBER OF CARBON ATOMS FOR SOLVENT EFFECTIVENESS

Polar group	Number of C atoms per group	Polar group	Number of C atoms per group
$-\overset{\vert}{\underset{\vert}{P}}O_4$	6	$-NO_2$	2
$>CO_3$			2
$-C{=}O$ / $-O-$ / $-C{=}O$	4	NH_2	2
		SO_4	>2
$-OH$	3	$>NH$	1
$-\overset{\vert}{C}O$	3	$-O-$	1
$-COO-$	3	$-S-$	1
$-CN$	3	$>N-$	1
$-CHO$	2	$>C{=}C<$	1
$-COOH$	2		

polar solvent In the fractionation of oils, furfural can be used either alone or as one component of a two solvent system, according to the temperature chosen for operation. A suitable and cheap nonpolar solvent is ordinary petroleum naphtha

While a considerable degree of fractionation may be obtained by batch operation, as in the examples detailed above, the efficiency of the process is much improved by producing continuous counterflow mixing of the oil and solvents in an extraction tower, and refluxing a portion of the extract Liquid–liquid extraction embodying the reflux principle is entirely analogous to rectification in fractional distillation In the case of single solvent extraction, reflux is produced by reintroducing a portion of the extract oil (after it is freed of solvent) with the feed oil In systems operating with two solvents, adequate reflux may be obtained by introducing a suitable quantity of the nonpolar solvent at the lower, or extract discharge end of the tower, and permitting it to flow countercurrent to the extract phase

The principles applicable to fractional distillation all have their counterpart in liquid–liquid extraction Just as an appreciable difference in the vapor pressures of two components will permit their separation by distillation (the completeness of separation depending upon the size of the fractionating column and the capacity at which it is operated), so will a difference in the affinity of two components for a solvent permit their separation by liquid–liquid extraction In the case of fats and oils, the attainable degree of separation is limited by the mixed nature of the glycerides However, the degree to which the separation of fatty acids or their mono esters may be carried is defined principally by economic considerations relating to the size of the extraction towers and the practicable limits to which refluxing may be carried

Since the extraction rate in liquid–liquid extraction is controlled by a process of molecular diffusion between adjacent layers of two immiscible liquids, the methods employed in calculations of absorption, distillation, or other diffusion processes, are likewise applicable to calculations for the design of extraction towers A recent general review of methods for design calculations in liquid–liquid extraction has been presented by Elgin [13] Calculations for the specific system soybean oil–furfural have been made by Ruthruff and Wilcock [14] However, according to Goss,[15] the equilibrium diagram upon which the calculations are based is incorrect, because of failure to extend it to iodine values higher than one equilibrium stage above the iodine value of the original oil

[13] J C Elgin *Chem & Met Eng*, 49, 110–116 (1942)

[14] R F Ruthruff and D F Wilcox, *Trans Am Inst Chem Engrs*, 37, 649–667 (1941)

[15] W H Goss, private communication to the author

(b) *Liquid–Liquid Extraction in Practice*

Commercial liquid–liquid extraction units for fatty materials have but recently come into use,[16] and details of their construction and operation are not generally available, hence the present description of the process must be confined to somewhat general terms. A suitable extraction apparatus consists of a tower, preferably of stainless steel, 50 to 100 feet in height, insulated, and packed with Raschig rings or other suitable packing material. The diameter of the tower will depend upon the capacity desired. Ordinarily, the combined feed and reflux oil passed through the column may amount to about 1200 to 1500 pounds per hour per square foot of cross sectional area. At a 9:1 reflux ratio, therefore, the capacity in terms of feed oil will amount to about 120 to 150 pounds per square foot per hour. Hence for a column to have a capacity of one tank car (60,000 pounds) of oil per day, it must have a cross sectional area of about 16 to 21 square feet or a diameter of about 4.5 to 5 feet.

In addition to the extraction column proper, a complete liquid–liquid extraction plant of course requires suitable evaporators and condensers for recovery of solvent, as well as feed heaters, circulating pumps, metering devices, and miscellaneous other accessory equipment.

The general design and operation of extraction columns utilizing both single and dual solvents is indicated diagrammatically in Figure 96. As indicated previously, the temperature of operation will depend somewhat upon the nature of the fatty material and the solvents used; it may vary from about 100°F. to about 175°F. Reflux ratios and ratios of solvent to oil or other fatty material will of course vary considerably, but will generally be in the range of about 2:1 to 10:1, and 4:1 to 10:1, respectively.

The liquid–liquid extraction process has to date been of principal interest as a means of obtaining quick drying fractions suitable for varnishes, enamels, etc. from oils of poor or moderate drying properties. In the fractionation of vegetable oils a rather greater degree of separation has been obtained than would perhaps be predicted from the well known Hilditch principle of even distribution of the fatty acids in the glyceride molecules. Thus, for example,[15] soybean oil with an iodine value of 133 may yield 30% of an extract with an iodine value of 173 and 70% of a raffinate with an iodine value of 116, or raffinate and extract differing in iodine value by as much as 57 units. In the fractionation of linseed oil or fish oils even greater differences can be produced in the iodine values of

[16] See the following: S. E. Freeman (to Pittsburgh Plate Glass Co.), U. S. Pats. 2,200,390–91 (1940); 2,278,309 and 2,291,461 (1942); 2,313,636 and 2,316,512 (1943). A. H. Batchelder (to Standard Oil Co. of Calif.), U. S. Pat. 2,285,795 (1942). W. H. Goss and H. F. Johnstone (to Secretary of Agriculture), U. S. Pat. 2,290,609 (1942). J. D. Jenkins (to Pittsburgh Plate Glass Co.), U. S. Pat. 2,320,738 (1943).

the two fractions The fractionation of glycerides is covered by apparently conflicting patents issued to Freeman and to Batchelder Fractionation of fatty acid mixtures by liquid–liquid extraction is covered by the patents of Freeman The patent of Goss and Johnstone covers the fractionation of methyl esters or other mono esters

A new liquid–liquid extraction process recently developed in the United States employs liquid propane as a solvent, with the extraction operation being conducted at temperatures approaching the critical temperature of the propane, to render it incompletely miscible with the oil Fractionation

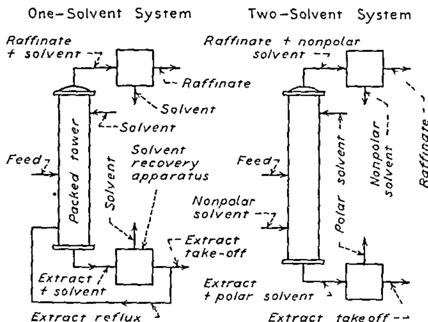


FIG 96 —Liquid-liquid extraction processes for single solvent and double solvent systems

of oils into portions of different unsaturation may be achieved, but the process appears chiefly noteworthy for its remarkable effectiveness in the segregation of pigments, vitamins, and other nonglyceride constituents from the oils

Behr[17] achieves a segregation of the highly unsaturated, polymerizable glycerides of fish oils by polymerizing the oils, and extracting the polymerized oils with ketones or higher alcohols to remove the relatively saturated, unpolymerized portions A similar treatment is applied to linseed oil to produce the so called "Tekaols"[18]

[17] O M Behr (to Vegetable Oil Products Co), U S Pat 2,239,692 (1941)

[18] E Rossmann, *Angew Chem* , 50, 246–248 (1937)

4. Fractional Distillation

(a) *Theory and Practice*

Fractional distillation is not generally applicable to fats and oils as such, but only to the more volatile fatty acids and their monoesters Glycerides may be distilled by molecular distillation, but the process is relatively expensive and fractionation is poor, hence it is chiefly valuable as a means of separating vitamins or other nonoil constituents from commercial fats and oils

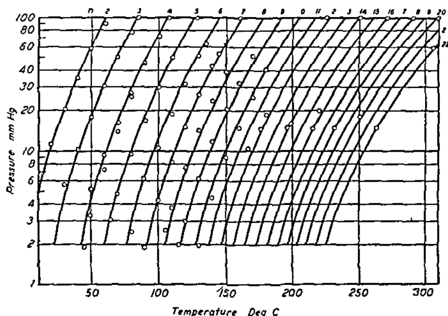


Fig 97 —Vapor pressure of fatty acids (n = number of C atoms in acid)[19]

Whereas fractional crystallation and liquid–liquid extraction effect a fractionation of fatty materials upon the basis of their relative degree of unsaturation, the fractionation produced by distillation is almost entirely according to molecular weight or chain length Fatty acids or esters of a given chain length exhibit but very slight differences in volatility with different degrees of unsaturation It is a matter of extreme difficulty, for example, to produce even a partial separation of oleic and stearic acids by distillation in efficient laboratory columns, and commercially such a separation is wholly impracticable On the other hand, there is a marked difference in volatility in any two fatty acids of different chain length In the range of temperatures within which distillation is practicable, the vapor pressure of a fatty acid at a fixed temperature is more than doubled for each decrement in chain length of two carbon atoms (Fig 97)

[19] Attributed by E Schlenker to W Gensecke See G Hefter and H Schönfeld, *Chemie und Technologie der Fette und Fettprodukte* Vol II, Springer, Vienna 1937, p 503

While fractionation of a fatty acid mixture by distillation cannot be accomplished upon the basis of differences in unsaturation alone, it so happens that in many cases distillation of the mixed acids from an oil will yield fractions differing greatly in iodine value, due to the particular composition of the oil Thus for example, the saturated acids of cottonseed oil, soybean oil, and many other vegetable oils consist preponderantly of palmitic acid, a C_{16} acid Separation of palmitic acid from the mixed fatty acids of these oils will leave a residue consisting almost entirely of oleic and linoleic acids, and hence considerably more unsaturated than the original oil Soybean oil fatty acids so fractionated are produced commercially with an average iodine value of 147 5, whereas the average iodine value of the original acids is about 136

Fish oils may be fractionated to an even greater extent, inasmuch as their highly unsaturated fatty acids contain 20 and 22 carbon atoms, and hence are easily separable from the less unsaturated C_{14}, C_{16}, and C_{18} acids Mixed sardine oil fatty acids (with an iodine value of about 195) are commercially distilled to produce a fraction with an iodine value as high as 250 [20]

A technique highly effective in separating polymerizable from relatively saturated and hence nonpolymerizable fractions of fatty acids or mono esters consists of heat treating the mixed acids or esters to the point of dimerization of the reactive members, and separating the resulting mono mers and dimers by fractional distillation [21]

From coconut oil fatty acids or other fatty acid mixtures comprising a variety of saturated acids of different chain length it is easily possible to prepare by distillation fractions consisting substantially of single fatty acids Thus caprylic, capric, lauric, myristic, palmitic, and stearic acids are all prepared commercially with purities of 90% or better It is to be noted that fractionally distilled stearic acid is somewhat different from ordinary commercial "stearic acid," which actually is a mixture of stearic acid with an equal or greater proportion of palmitic acid

(b) *Distillation for the Purification of Fatty Acids*

Since commercial fatty acids are commonly derived from the lowest grades of fats, including very dark tallows and greases, and foots remaining from the refining of vegetable oils, they require purification Purification of the crude fatty acids is effected by distillation, which not only accomplishes the removal of pigments and other relatively nonvolatile impurities, but also separates the acids from any residue of unhydrolyzed oil remaining from the splitting operation

Fatty acid distillation is invariably carried out under reduced pressure,

[20] D V Stingley, *Ind Eng Chem* 32, 1217–1220 (1940)
[21] See T F Bradley and W B Johnston *Ind Eng Chem*, 32, 802–809 (1940)

and with the aid of stripping steam The ordinary temperature range in distillation is from about 450° to 500°F The *maximum permissible* temperature depends principally upon the possibility of polymerizing the acids to an excessive degree A highly unsaturated stock cannot be distilled at as high a temperature as a stock of low iodine value, and if the distillation equipment is so designed as to require the stock to be kept hot for a long period it cannot be operated at as high a temperature as equipment in which the acids are heated and distilled more quickly Low molecular weight acids are naturally distilled at lower temperatures than acids of high molecular weight

At high temperatures fatty acids are very corrosive to ordinary carbon steel The most suitable material for the construction of stills is a Type 316 or other molybdenum-stabilized stainless steel Ordinary 18 8 stainless steel is said to be not much more resistant than ordinary steel

Formerly the most common type of fatty acid still consisted simply of a direct fired pot equipped with a source of superheated steam, condensers, and some sort of vacuum pump Recent installations, however, have consisted very largely of continuous stills The latter offer a number of advantages over batch stills, including an improved yield of distilled acids In continuous distillation the time that the fatty acids are in the apparatus is much reduced, and there is consequently less loss from polymerization The residue of unsplit fat and polymerized fatty acids, known as still or stearine pitch, is used in floor tiling, electrical insulation, industrial paints, etc In batch stills operating on some stocks it may represent a substantial part, *e g*, 10% or more, of the total product

One of the earliest and most successful forms of continuous fatty acid stills was devised by Wecker [22] In the Wecker system, vaporization of the acids is effected in a closed, flat, rectangular, traylike chamber, divided internally into compartments, and heated from beneath by a large number of gas burners The feed stock, preheated in a heat exchanger with steam, flows horizontally through the compartments of the chamber in series It is either stripped or partially stripped of fatty acids during its passage through the chamber, and discharges from the end of the chamber remote from the intake as stearine pitch, or incompletely distilled stock, the residue passing successively to a cooler, a receiving tank, and a discharge pump

The stripping medium, which is injected into each of the compartments within the vaporization chamber, consists of wet steam, produced by bringing together streams of superheated steam and cold water According to the Wecker patent claims, water may alternatively be atomized into nitrogen or other inert gas What advantage accrues from the use of a

[22] E Wecker, Ger Pat 397,332, Brit Pat 213,267 (1923), U S Pat 1,622,126 (1927)

stripping medium bearing a fog of water, rather than ordinary saturated or superheated steam, is not clear

In the Wecker still, as in other fatty acid stills, the vapor stream of mixed fatty acids and steam is first partially cooled, to condense and remove the fatty acids and then further cooled, to condense the steam The vapor pressures of water and fatty acids are sufficiently different that there is no difficulty in selectively condensing the two, although there is some tendency for the steam to carry a fog of liquefied acids, after the latter have been condensed Various devices are employed to assist in the mechanical separation of the steam and the entrained acids The separated acids discharge to a receiving tank from which they are continuously pumped out of the system Vacuum is maintained on the system by a positive displacement pump placed beyond the steam condenser

The vacuum obtained in the Wecker apparatus depends upon the temperature and vapor pressure of the condenser water, hence the absolute pressure will not usually be lower than about 15 to 30 mm The time required for the material to pass through the apparatus is said to ordinarily be 10 to 15 minutes This system is not adaptable to close fractionation of fatty acid mixtures, although some degree of fractionation may be obtained by using different units in series, or by passing material repeatedly through the same unit at successively increasing temperatures It is very suitable for the steam refining of oils

Late installations of fatty acid stills in the United States have employed ordinary tray and bubble cap towers with the feed stock and the stripping steam being heated by Dowtherm vapor Dowtherm heating is highly advantageous in comparison with direct firing, as Dowtherm vapors can be condensed at a temperature only slightly above that desired in the feed stock, and thus overheating and polymerization of acids in stagnant films or "dead spots" is entirely avoided

Complete equations for the calculation of problems in both batch and continuous steam distillations have been given by Garber and Lerman [23]

(c) *Equipment for Fractional Distillation of Fatty Acids*

Equipment for the fractional distillation of fatty acids, as described by Potts and McKee,[24] is shown schematically in Figure 98 The essential parts are a vaporizer, *1*, consisting of vertical tubes externally heated by condensing Dowtherm, a fractionating column, *2*, fitted with conventional trays and bubble caps, a secondary stripping column, *3*, similarly fitted, a combined receiving tank and spray separator, *4*, a vacuum producing apparatus, *5*, consisting of steam ejectors and barometric condensers, and

[23] H J Garber and F Lerman *Trans Am Inst Chem Engrs*, 39, 113-131 (1943)

[24] R H Potts and J E McKee (to Armour & Co) U S Pats 2,224,925 and 2,224,984 (1940)

various interconnecting lines, pumps, and condensers. The entire system operates under a vacuum, the actual pressure in any part of the system depending upon the pressure drop from that part of the system to the ejectors. An absolute pressure of about 5 mm. is maintained at the top of the main column, but the pressure at the vapor inlet may not be less than about 40–50 mm., and that at the bottom of the vaporizer may be about 200–250 mm.

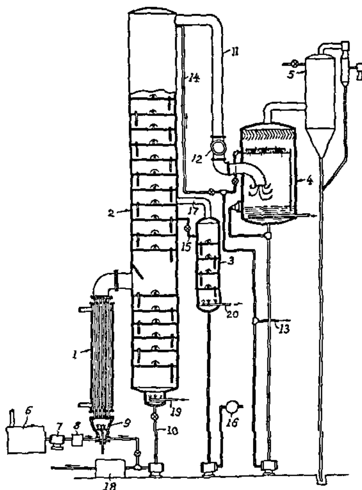


Fig. 98 —Apparatus for fractional distillation of fatty acids.[24]

From feed tank *6*, the fatty acid stock is transferred by pump *7*, through preheater *8*, into vaporizer *1*. Superheated steam at about 500°F. is injected into the bottom of the vaporizer at *9*, the amount of steam corresponding to 0.05 to 0.25 pound per pound of fresh feed stock. The vaporizer also communicates with the bottom of the main column through line *10*, so that a portion of the material taken from the bottom, consisting principally of unsplit oil or high molecular weight fatty acids, can be recycled to the vaporizer. The flow of recycled material is so maintained that stock is taken from the bottom of the column at about 500°F.,

and returned to the column at about 550°F. This recycling of material supplies sufficient heat to the column to reboil the reflux necessary for good fractionation in the column

The highest boiling acids, *e g*, the C_{16} acids in a mixture of C_{16}, C_{18}, C_{20}, and C_{22} acids, are taken from the top of the main column through line *11*, and condensed in condenser *12* As cooling is only carried to about 150°F in this condenser, the steam does not become liquid, but is carried onward, through the spray separator *4*, and finally condensed and discharged from the barometric condenser A portion of the liquefied acids is taken from tank *4* and withdrawn from the system at *13*, but the greater portion is returned to the top of the column as reflux, through line *14* A reflux ratio of at least 4 1 is recommended

The tray containing the greatest concentration of medium boiling acids in the main column, *e g*, C_{18} acids of the above series, is tapped through line *15*, and a portion of the acids reaching this tray is diverted to the top of secondary column *3* C_{18} acids are withdrawn from the bottom of this column through cooler *16*, whereas C_{16} or other more volatile acids are stripped out and returned through line *17* to the main column

The least volatile materials obtained in the operation, which may consist largely of unsplit oil and polymerized acids or in some cases of C_{20} and C_{22} acids, are withdrawn through cooler *18* Additional stripping columns may be provided for further separations as for example to separate C_{20} and C_{22} acids from unsplit oil, polymerized material and other nonvolatile components of the stream withdrawn from the bottom of the main column

In addition to that injected in the vaporizer, superheated steam is also injected in the bottom of the columns, at *19* and *20*, respectively It is recommended that the total steam injected be less than one half, and preferably less than one fourth the weight of the feed stock entering the apparatus

In a later patent, Potts[23] describes fractional distillation equipment of slightly different design in which steam is employed *only in the first stripping column*, and distillation is carried out in the main fractionating column without the aid of steam This method of operation is said to result in unusually sharp separation of the different fatty acids, and to be preferable to that outlined above

(d) *Commercial Molecular Distillation*

Large scale molecular distillation[25] is principally useful for producing vitamin A concentrates from fish liver oils and vitamin E (tocopherol) concentrates from vegetable oils, although other nonglyceride substances of

[23] R H Potts (to Armour & Co) U S Pat 2 322 056 (1943)

[25] For a recent review of commercial molecular distillation see K C D Hickman, *Chem Revs*, 34, 51–106 (1944)

possible commercial value, including sterols[27] and hydrocarbons[28] can also be separated from oils by this method of distillation

If the vitamins are stripped from the oils by molecular distillation, the residual oil is of course available for any other desired use, whereas this is not the case if the oil is saponified and the vitamins extracted from the unsaponifiable material Also, according to Hickman and co workers,[29] vitamin A concentrates separated from fish liver oils by molecular distillation are more stable and retain their potency longer than concentrates prepared by saponification of the oils, due to the fact that the vitamin in the former remains esterified, whereas that in the latter is converted to the more easily oxidized free alcohol

The conditions required for efficient molecular distillation on a laboratory scale must be duplicated in commercial distillation In other words, a thin and uniform film of the thoroughly degassed and turbulently moving oil must be continuously passed in proximity to a relatively cold condensing surface, and the space between the oil film and the condenser must be maintained at a vacuum of the order of 0 001 mm , or about one millionth of an atmosphere, in order to permit free passage of molecules of the distillate between the two surfaces

The design of equipment capable of fulfilling the above conditions, and of presenting large evaporating and condensing surfaces within a reasonably compact apparatus, presents considerable difficulty An ordinary laboratory still of the falling-film type translated to large dimensions is extremely lacking in compactness, and in addition, films moving under the force of gravity are insufficiently thin and insufficiently turbulent to provide the most rapid and efficient distillation The molecular stills designed by Hickman[30] overcome these difficulties by employing rapidly revolving plates inside gastight housings for spreading the oil film The oil, fed to the center of the plates, is spread thereon in a uniform film, and discharged to the periphery of the plates, by centrifugal force The stripped oil is collected in gutters attached to the rotating plates, while the material distilling from the oil is condensed on the inner surface of the housing above the rotors and drains to the bottom of the housing

By the centrifugal method, oil films are produced which are said to be no more than 0 01–0 1 mm in thickness, as compared with 0 2–1 0 mm in the case of falling films[26,31] The maintenance of a very thin film favors

[27] K C D Hickman, *Ind Eng Chem* , 32, 1451–1453 (1940)

[28] J G Baxter (to Distillation Products, Inc) U S Pat 2 169,192 (1939)

[29] See, for example, K C D Hickman and A O Tischer, U S Pat 2,169,195 (1939)

[30] Various forms of centrifugal stills, all embodying the same basic principle are described in U S Pats 2,210,927–28, 2,218 240, 2 234,166, 2,249,526, and 2,298,377, all issued to K C D Hickman and assigned to Distillation Products, Inc

[31] K C D Hickman and J C Hecker (to Distillation Products, Inc), U S Pat 2,249,524 (1941).

rapid evaporation of the oil, due to the relatively large surface presented, and the rapid flow of oil across the spinning plate presumably introduces a high degree of turbulence, which is likewise favorable to rapid impoverishment of the oil of distillable substances. The oil may be heated just prior to being introduced upon the plate (or heated on the plate) and cooled immediately after it is discharged, hence the period in which it is maintained at a high temperature may be reduced to a matter of a few seconds (it is usually on the plate less than one second). Since the above mentioned vitamins distill in the range of about 170° to 270°C., there is a possibility of heat altering some of the constituents of the oil if the period during which the oil is heated is prolonged.

Stills are in use which have rotors 14 inches, 32 inches, and 60 inches in diameter, and which will respectively handle about 5, 25, and 100 gallons of feed oil per hour. An installation of 21 centrifugal stills, 32 inches in diameter, is said to have a capacity of about 40,000 gallons of oil monthly, in the production of vitamin A concentrates.[32] The production of concentrates high in tocopherol content involves multiple distillation, a product containing 40% to 80% tocopherols being obtained in this way.

Vacuum for commercial molecular distillation is produced by condensation pumps employing an organic liquid of low vapor pressure, which are operated in conjunction with mechanical vacuum pumps or multistage steam ejectors.[26]

[32] K. C. D. Hickman, *Chem. Eng. News*, 20, 1561–1562 (1942).

CHAPTER XXI

FAT SPLITTING, ESTERIFICATION, AND INTERESTERIFICATION

1. Introduction

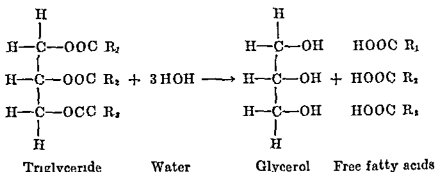
The operations of fat splitting, in which fat is hydrolyzed to yield free fatty acids and glycerol, of esterification, in which free fatty acids are recombined with glycerol or combined with another alcohol, and of interesterification, in which esterified fatty acids and alcohols are caused to undergo intermolecular rearrangements—are logically considered together. Similar reactions are involved in these operations, and the different reactions are in general catalyzed by the same substances.

Fat splitting has been extensively practiced for nearly a century, for the production of fatty acids for soapmaking and the manufacture of candles. Esterification and interesterification processes have but recently begun to receive attention, but can be expected to assume increasing importance in the future. These processes are more or less essential tools in the manufacture of the new, so called "tailor made" fats and oils, and have other important industrial applications.

2. Fat Splitting

(a) General Considerations

The over all reaction in fat hydrolysis or fat splitting is as follows:



However, the reaction naturally proceeds in stages, with the fatty acid radicals being displaced from the triglyceride molecule one at a time, so that an incompletely split fat will contain both mono and diglycerides, as well as triglycerides. It was demonstrated by Kellner[1] that the extent to which mono- and diglycerides are formed is considerably variable ac

[1] J Kellner, *Chem Ztg*, 33 453 (1909) 33, 661 662 (1909)

cording to the conditions under which splitting is carried out. Mono- and diglycerides corresponding to as much as 3.5% excess combined glycerol were produced in fat partially split in an autoclave. Less mono- and diglycerides were produced in splitting by the Twitchell method, and still less in fermentative fat splitting. No mono- or diglycerides were produced by partial saponification of a fat with a strong alkali.

Hydrolysis is accelerated by mineral acids, a number of metallic oxides or hydroxides, and various organic catalysts. In practice, the effectiveness of a catalyst is dependent not only upon its fat splitting action *per se*, but also to a great extent upon its ability to promote emulsion between the oily and aqueous phases undergoing reaction. The establishment of a large water–oil interface is very necessary, because of the limited mutual solubility of the two phases. With ordinary catalysts, splitting does not become rapid except at somewhat elevated temperatures, but fats are readily hydrolyzed at ordinary atmospheric temperatures by certain lipolytic enzymes of plant and animal origin.

The following data, due to Lascaray,[2] are roughly indicative of the temperature coefficient of the fat-splitting reaction. The times required at different temperatures to free 50% of the fatty acids in a tallow subjected to treatment in an autoclave with 60% water and 0.5% sodium hydroxide were approximately as follows:

Temperature °C	Time, hours
220°	0.5
200°	0.9
185°	2.2
170°	4.2
150°	9.0

The accelerating effect of increasing the temperature is due partly to the positive temperature coefficient of the reaction, and partly to the fact that water becomes more soluble in fats and fatty acids as the temperature is raised. It is Lascaray's conclusion that only a minor part of the splitting occurs at the oil–water interface, and that hydrolysis is essentially a homogeneous reaction, occurring between fat and dissolved water in the oil phase. According to this view, metallic oxide catalysts function partly through their effect on the solubility of water in fat. It was demonstrated that the presence of 0.5% zinc oxide, for example, increased the solubility of water in fatty acids at 100°C. from 1.37% to 2.78%.

The fat-splitting reaction is reversible, hence a point of equilibrium between hydrolysis and re-esterification will eventually be reached, unless by some means the liberated glycerol is removed. In practical operation of the process a high degree of splitting is desired, and continuous removal of the glycerol is generally not feasible. The effect of operating conditions on

[2] L. Lascaray, *Fette u. Seifen*, 46, 628–632 (1939).

the pomt of equilibrium is, therefore, a matter of some concern It has been shown by Kaufmann and Keller[3] and confirmed by Lascaray, that the equilibrium pomt is determined solely by the concentration of glycerol in the water phase, and is independent of the temperature, and the kind and the concentration of catalyst It is pointed out by the former authors that the indifference of the equilibrium constant to temperature is an indication that the heat of the reaction is zero In practice, splitting may be made more complete by conducting the operation in two or more stages, and removing the water–glycerol solution and substituting fresh water after each stage

TABLE 159
THEORETICAL GLYCEROL CONTENT OF NEUTRAL FATS AND OILS

Fat or oil	Saponification value	Glycerol content %
.	198	10 83
	191	10 45
	248	13 57
Coconut oil	253	13 84
Rapeseed oil	175	9 57

The maximum theoretical amount of glycerol recoverable from a neutral fat may be calculated from the saponification value of the latter by the following formula

$$\text{Per cent glycerol} = (\text{saponification value})\ (0\ 0547)$$

In plant practice the actual amount recovered will be somewhat less than the calculated amount, due to the circumstances that splitting is never complete, and that the fats split are seldom, if ever neutral, but invariably contain some quantity of fatty acids which are uncombined with glycerol In the case of low-grade tallows, greases and palm oils the free fatty acids may amount to a considerable part of the total acids The theoretical glycerol contents of neutral fats and oils of different saponification values are given in Table 159

(b) *Fat Splitting by the Twitchell Method*

The most commonly employed method of fat splitting depends upon the use of catalytic agents of a type first used and described by Twitchell[4] The first Twitchell reagents were prepared by sulfonating the reaction product of a fatty acid and benzene or naphthalene In the case of benzene, the produce presumably has the formula (R) C_6H_4 (SO_2OH) The

[3] H P Kaufmann and M C Keller, *Fette u Seifen* **44**, 42–47, 105–107 (1937)
[4] E Twitchell, U S Pat 601,603 (1898), *J Am Chem Soc*, **22**, 22–26 (1900)

original Twitchell reagents have been improved by the substitution of cymene, anthracene, etc for benzene or naphthalene, and by various other structural modifications, the reagent in most common use in the United States at the present time is not prepared from fatty acids, but is a sulfonated petroleum product of the "Kontakt" type

Twitchell reagents are strongly surface active, and part of their effectiveness is undoubtedly due to their ability to promote the formation of emulsions It is to be noted that even though fat splitting may occur largely as a result of reaction between oil and water dissolved in the oil, it is nevertheless necessary to establish a large oil-water interface in order to maintain the rate of solution at a high level

The Twitchell process has attained much of its popularity as a result of its requiring relatively simple and inexpensive equipment The operation is carried out in tanks at atmospheric pressure, wooden, lead lined, or Monel metal lined tanks are employed, since the process requires some degree of acidity in the aqueous phase Often the fatty stock to be subjected to Twitchellization contains considerable amounts of albuminous material and other impurities These have a pronounced poisoning effect on the catalyst,[5] and hence must be removed It is more or less general practice to subject the fat charge to a period of boiling with dilute sulfuric acid for this purpose before splitting is started Fat stocks of particularly poor quality are often acid refined with strong sulfuric acid before they are split

The acid washed fat is mixed with about 25-50% of its own weight of water and 0 75-1 25% of its weight of Twitchell reagent, splitting is carried out by boiling the mixture with open steam over a period of about 36 to 48 hours The tanks are usually provided with covers, to minimize contact of the charge with air, and consequent excessive darkening of the fatty acids Even with the most careful operation there is invariably some darkening of the acids This darkening, the long time required, and the rather high consumption of steam, constitute the chief disadvantages of the Twitchell method

The splitting is carried out in at least two, and often in three, or even four stages, with the liquor or "sweet waters" containing the liberated glycerol being drawn off at the end of each stage, and replaced with fresh water, or more commonly, with weaker sweet waters from a previous boil, countercurrent operation being maintained throughout the series of boils Where two periods of boiling are employed, about 85% to 90% of the total splitting will take place in the first stage, and the remainder will take place in the second stage Typical four stage operation will distribute splitting in the four stages in the respective proportions of about 60%, 25%, 10% and 5% Smaller amounts of water are used if the operation is con-

[5] R B Trusler, *J Oil & Fat Ind*, **8**, 141-143 (1931)

ducted in a number of stages The degree of splitting obtained will depend upon the number of stages and the time allotted for the operation, ordinarily about 95% to 98% of the fat will be hydrolyzed A higher degree of splitting requires an impracticably long time, and produces excessively weak glycerol solutions

Although an emulsion is produced during boiling, this will generally break when steaming is discontinued If a persistent emulsion is formed, a little sulfuric acid may be added to break it The operation is finished by adding fresh water to the fatty acids and boiling to wash out the mineral acid remaining Some operators recommend the addition of barium carbonate to neutralize the residual sulfuric acid

(c) *High Pressure Fat Splitting Employing a Catalyst*

The high pressure or autoclave method of fat splitting is actually the oldest method employed on a commercial scale, patents covering the process date back as far as 1854 The autoclave method suffered some *decline in popularity after the introduction of the Twitchell process, but* has lately experienced something of a revival It is now being used to a considerable extent for splitting higher grade stocks, to produce light colored fatty acids which do not require distillation In addition to producing lighter acids, the autoclave process is much more rapid than the Twitchell process

The catalysts used in autoclave splitting consist of various metallic oxides and hydroxides, of which zinc, magnesium, and calcium oxides are the most commonly used Of these, zinc oxide is the most active According to the experiments of Lascaray,[2] different catalysts are decreasingly active in the following order ZnO, MgO, CaO, LiOH, NaOH, KOH NH_4OH About 2–4% of catalyst is used, based on the weight of the fat, and often a fraction of one percent of zinc dust is also added The zinc does not act as a catalyst, but through its reducing *action, or otherwise, it* improves the color of the fatty acids

The autoclaves are built in the form of tall cylinders, which may be as much as 4 to 6 feet in diameter, and 20 to 40 feet in height The older autoclaves were usually constructed of copper, but autoclaves are now commonly made from corrosion resistant nickel–chrome alloys The autoclaves are insulated, and equipped with lines for the injection of steam but no mechanical agitators

In operation, the autoclave is charged with the fat, the catalyst, and water equivalent to about 30–60% of the weight of fat Steam is blown through the mass to displace air in the headspace and dissolved air in the fat and water, and the autoclave is then closed, and steam is admitted to raise the internal pressure to 75 to 150 pounds The steam is injected at

the bottom, condensation of steam within the vessel plus the venting of a small amount of steam maintains a sufficient steam flow to keep the charge agitated About 6 to 10 hours are required to bring about a splitting of 95%, or better After the desired degree of splitting is obtained, the contents are blown out into a settling tank, where the separated fatty acids are drawn off from the water–glycerol liquors The fatty acids must then be treated with sulfuric acid or other mineral acid, to decompose the soaps formed by the catalyst, after which they are washed free of mineral acid

There are in the literature virtually no modern data pertaining to the details of autoclave fat splitting, but the above-mentioned laboratory data of Lascaray are of some interest, since they illustrate the relative effect

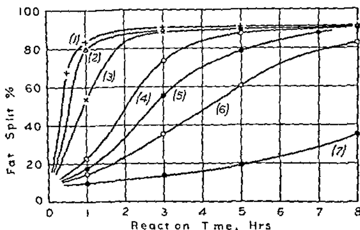


FIG 99 —Autoclave splitting of tallow with 60% water (1) at 220°C with 0 5% NaOH as a catalyst, (2) at 185°C, 0 51% ZnO, (3) 200°C, 0 5% NaOH, (4) 185°C, 0 5% NaOH, (5) 185°C, no catalyst, (6) 170°C, 0 5% NaOH, (7) 140°C, 0 5% NaOH [2]

of different factors on the reaction The effect of temperature and the order of effectiveness of the different catalysts have been mentioned above In Figure 99 are shown the results of a series of tests carried out at different temperatures on tallow, using 60% of water and 0 5% sodium hydroxide as a catalyst The same figure also shows the results of a corresponding test at 185°C in which 0 51% zinc oxide was used as a catalyst, and a test at this temperature without a catalyst

The temperatures employed in these tests correspond to gage pressures of steam as follows 140°C, 38 pounds, 170°, 100 pounds, 185°, 148 pounds, 200°, 210 pounds, 220°, 322 pounds

The degree of splitting obtained at equilibrium was independent of the temperature, but increased slightly with increased catalyst, because of the displacement of the equilibrium by the combination of fatty acids with the

catalyst, to form soaps In Figure 100 the percentage of fat split at the end of 8 hours at 185°C with 0 5% sodium hydroxide is shown graphically, in terms of the percentage of water used, on a fat basis Virtual equilibrium was attained in all cases at the end of this reaction time

Continuous high-pressure fat-splitting systems have been devised For a description of a commercially 32[6] Autoclave fat splitting with T at temperatures below those required with lime, zinc oxide, etc, but the necessity for maintaining the system acid so limits the materials from which the autoclave can be constructed as to render the method more or less impracticable

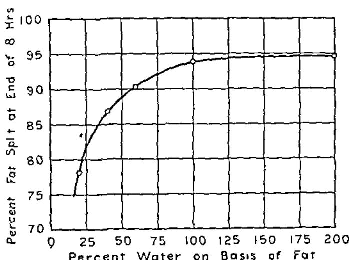


FIG 100 —Effect of percentage of water on the point of equilibrium in the auto clave splitting of tallow at 185°C with 0 5% NaOH as a catalyst[2]

(d) *High Pressure Fat Splitting without the Aid of a Catalyst*

Autoclave fat splitting without the aid of a catalyst is relatively little practiced, although one large American manufacturer is reported to be currently employing this process By using a special autoclave fabricated from stabilized stainless steel, and equipped with an efficient mechanical agitator, rapid splitting is said to be accomplished at about 450°F, with the production of light colored fatty acids, and a very pure glycerol solution However, the high temperature required for this method of splitting renders it unsuitable for highly unsaturated, easily polymerizable stocks

[6] See also U S Pats 2,139,589 (1938) and 2,221,799 (1940) (to M H Ittner, assigned to Colgate Palmolive Peet Co), U S Pat 2,281 534 (1942) (to W Davey and M H Ittner, assigned to same company), and U S Pat 2,156,863 (1939) (to V Mills, assigned to Procter & Gamble Co)

(e) *Enzymatic Fat Splitting*

Fat-splitting through the use of lipolytic enzymes[7] has been carried out on a commercial scale in the past, although it is doubtful whether this process is of much present importance

The enzyme preparation is usually obtained from castor beans The beans are ground with water, and the ground mass is centrifuged to remove solid material The resulting emulsion of water, oil, protein, etc , is then fermented at room temperature for 48 hours, after which it is ready for use

Splitting is carried out in open, conical bottom, lead lined tanks The fat is mixed with 30–40% of its weight of water, and about 6% of the ferment Sufficient acetic acid or other acid is added to bring the pH of the system to a value of about 5, and also manganese sulfate solution equivalent to 0 15–0 20% of the dry salt on the basis of the fat A temperature of 35°C is considered optimum, although reasonably rapid splitting is obtained at temperatures as low as 15°C or as high as 40°C Outside this range of temperatures the activity of the ferment falls off rapidly, hence the process is not adaptable to fats of high melting point

The mass in the tank is agitated, to form an emulsion, and then is held at the proper temperature for about 24 to 48 hours, with occasional stirring As in other fat splitting processes, hydrolysis takes place rapidly at first, and then more slowly, eventually reaching a point of equilibrium About 90% splitting is said to be practicable After splitting has taken place, the emulsion is broken by heat and the addition of a little sulfuric acid, after which the fatty acids may be drawn off and washed, in the usual way

3. Re-esterification of Fatty Acids with Glycerol or Other Alcohols

The re esterification of fatty acids and glycerol is exactly the reverse of fat splitting It is carried out by reacting equivalent quantities of acids and glycerol at an elevated temperature, while maintaining a vacuum on the reaction vessel to continuously remove the water which is formed The reactants are not miscible in all proportions, hence the mixture must be stirred A steam heated condenser must be inserted in the vacuum line, to condense and return glycerol vapors to the vessel, while permitting the escape of water vapor The vessel, like other processing equipment which must come into contact with hot fatty acids, is best constructed of molybdenum stabilized stainless steel, or other resistant alloy, to avoid damage to the vessel through corrosion, and metallic contamination of the product

[7] For additional information on enzymatic fat splitting, see E Schlenker in Hefter Schonfeld, *Chemie und Technologie der Fette und Fettprodukte* Vol II, Springer, Vienna, 1937, pp 485–491

TABLE 160

RELATIVE ACTIVITIES OF DIFFERENT INORGANIC ESTERIFICATION CATALYSTS[a]

Catalyst	FFA %	Catalyst	FFA %
Control no catalyst	16 1	NaOH	13 8
$AlCl_3$ $6H_2O$	17 1	Ni (hydrogenation catalyst)[b]	16 4
Al_2O_3[b]	15 4	$NiCl_2$ $2H_2O$	13 8
$CdCl_2$ $2H_2O$	11 0	$PbCl_2$[b]	12 0
$FeCl_3$ $6H_2O$	11 4	PbO	10 9
FeO[b]	13 9	$SbCl_3$	15 0
$HgCl_2$	15 0	$SnCl_2$ $2H_2O$	2 8
$MgCl_2$ $6H_2O$	13 7	$SnCl_4$ $5H_2O$	2 4
MgO	13 6	SnO_2[b]	15 1
$MnCl_2$ $4H_2O$	13 2	$ZnCl_2$	3 5
MnO_2	10 8	ZnO	11 8

[a] [illegible] pressure with an equivalent [illegible] catalyst per gram fatty acid [illegible] the end of 6 hours

[b] [illegible]

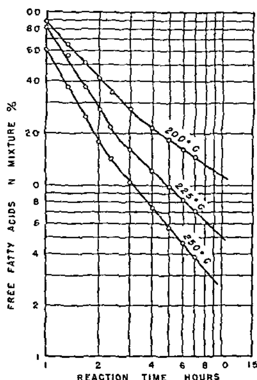


FIG 101 —Re esterification of peanut oil fatty acids with an equivalent quantity of glycerol and without a catalyst

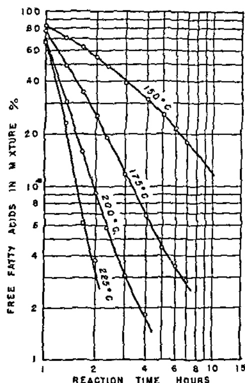


FIG 102 —Re esterification of pea nut oil fatty acids with an equivalent quantity of glycerol and with 0 18% $SnCl_2$ 2 H_2O employed as a catalyst

The reaction may be carried out without a catalyst, although without a catalyst it is impracticably slow at any temperature below about 225°C (437°F) It is catalyzed in general by the same reagents which promote

fat splitting. Among the inorganic catalysts, stannous chloride is the most effective, although zinc chloride is also quite active, and is much more effective than zinc oxide, or other oxides or hydroxides. In the presence of small amounts of stannous or zinc chloride (e. g., 0.2%) esterification may be completed in a reasonable time at temperatures as low as 150° to 175°C (302° to 347°F.). Certain aromatic sulfonic acids also are effective catalysts at low temperatures. Thus, for example Bhattacharya and Hilditch[8] were able to effect a substantially complete esterification of fatty acids and glycerol in the laboratory at 135° to 145°C., using 0.5% naphthalene-β-sulfonic acid as a catalyst. An excess of about 10–20% of fatty acids was employed, and 5–6 hours was allowed for the reaction.

Published data on the large-scale re-esterification of fatty acids and glycerol are wholly lacking. The results of laboratory experiments involving the use of various catalysts at different temperatures are shown in Table 160 and Figures 101, 102, and 103.

In order to obtain a product which consists entirely of triglycerides, with no mono- or diglycerides, it is necessary to provide a slight excess of fatty acids in the reaction mixture. However, it is possible to adjust the proportions of acids and glycerol so as to obtain an esterified product containing not more than 1–2% of free fatty acids. The catalysts may be completely removed from the esterified oil by ordinary alkali refining.

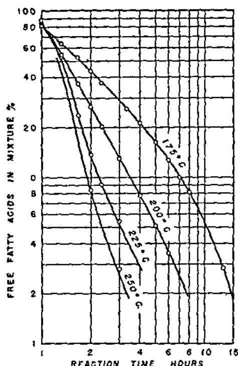


FIG. 103.—Re-esterification of peanut oil fatty acids with an equivalent quantity of glycerol and with 0.11% $ZnCl_2$ employed as a catalyst.

A patent covering the vapor-phase esterification of fatty acids and glycerol has been issued to German inventors.[8a] The operation is conducted in a specially designed apparatus, at a temperature of 220–230°C., and a pressure of 20–100 mm. Conde

glycerides serves to remove these from

are formed. Zinc and magnesium oxide catalysts are employed.

The esterification of fatty acids with ethylene glycol, mannitol, sorbitol, or other polyhydric alcohols, may be carried out similarly to esterifica-

[8] R. Bhattacharya and T. P. Hilditch, *Proc. Roy. Soc. London*, A129, 468–476 (1930).
[8a] I. G. Farbenindustrie A. G., Ger. Pat. 565 477 (1932).

tion with glycerol, however, in the case of ethylene glycol, the low boiling point of the alcohol somewhat limits the temperature and vacuum that can be employed. The esterification of fatty acids with monohydric alcohols, such as methyl and ethyl alcohol, is easily carried out by well known methods, and will not be considered here.

4. Interesterification Processes

As used here, the term "interesterification" refers to that class of reactions in which a fat or other material composed of fatty acid esters is caused to react with fatty acids, alcohols, or other esters, with the interchange of fatty acid groups.

(a) *Displacement of One Fatty Acid by Another*

If a neutral fat and uncombined fatty acids are heated together there is some tendency for interchange to occur between the combined and uncombined fatty acid groups, with the net result that the free acids partially replace the combined acids within the fat. Acids of low molecular weight readily displace high molecular weight acids at temperatures in the neighborhood of 200°C., at elevated pressures in the presence of esterification catalysts. This method is used by Schwartz[9] to introduce formic, acetic, or propionic acids into the glycerides of coconut oil, to produce a low melting oxidation resistant plasticizer for pyroxylin.

```
    H
    |
H—C—(high mol. wt. FA)
    |
H—C—(high mol. wt. FA) + (fatty acid of low molecular weight) ⟶
    |
H—C—(high mol. wt. FA)
    |
    H
```

```
    H
    |
H—C—(low mol. wt. FA)
    |
H—C—(high mol. wt. FA) + (fatty acid of high molecular weight)
    |
H—C—(high mol. wt. FA)
    |
    H
```

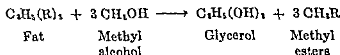
According to a patent issued to Barsky,[10] high molecular weight fatty acids in the free form can also be made to displace low molecular weight

[9] G. L. Schwartz (to E. I. du Pont de Nemours & Co.) U. S. Pat. 1 558 299 (1925).
[10] G. Barsky (to Wecoline Products Inc.), U. S. Pat. 2 182 332 (1939).

fatty acids from glycerides A fat containing low molecular weight acids, such as coconut oil or butterfat, is reacted with about one fourth to one half its weight of high molecular weight acids, such as those from cottonseed or palm oil at 260° to 300°C, without a catalyst, for 2 to 3 hours, and is finally distilled under reduced pressure until the free acids are substantially removed In the examples quoted, the saponification value of coconut oil was reduced from 258 to 245 by reaction with cottonseed oil fatty acids, and the saponification value of butterfat was reduced from 227 to 212 by reaction with palm oil fatty acids

(b) *Displacement of One Alcohol by Another*

Displacement of the glycerol in a fat by a low molecular weight alcohol, such as methyl or ethyl alcohol, is readily accomplished by the method described by Bradshaw and Meuly [11] The process is remarkable not only for producing methyl or ethyl esters directly from the fat, without the intervening step of hydrolysis, but also for taking place at low temperatures and requiring no alloy steel or other special corrosion resistant equipment Where methyl alcohol is used, the reaction is as follows



The reaction is carried out in any convenient open tank, which may be constructed from ordinary carbon steel The fat must be clean, dry, and substantially neutral It is heated to about 80°C (176°F), and to it is added commercial anhydrous (99 7%) methyl alcohol in which is dissolved 0 1–0 5% caustic soda or caustic potash The amount of alcohol recommended is about 1 6 times that theoretically required for the reaction, although the alcohol may be reduced to as little as 1 2 times the theoretical, if the operation is carried out in three steps Alcohol amounting to more than 1 75 times the theoretical quantity does not materially accelerate the reaction and interferes with subsequent gravity separation of the glycerol

After the addition of the alcohol the mixture is stirred for a few minutes, and is then allowed to stand The glycerol begins to separate almost immediately since it is virtually anhydrous and much heavier than the other liquids it readily settles to form a layer at the bottom of the tank Conversion of the oil to methyl esters is usually 98% complete at the end of an hour

The lower layer of glycerol contains not less than 90% of the glycerol originally present in the fat, the upper layer consists of the methyl esters,

[11] G B Bradshaw and W C Meuly (to E I du Pont de Nemours & Co), U S Pat 2 271 619 (1942) See also G B Bradshaw, *Soap & Sanit Chemicals*, 18, No 5, 23–24, 69–70 (1942)

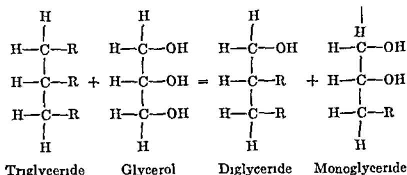
most of the unreacted alcohol and alkali, the remainder of the glycerol, and a very small amount of soap These various impurities are removed from the esters by successive washes with small amounts of warm water

The Bradshaw patent contemplates use of the methyl esters to make anhydrous soap by a continuous process The esters are easily saponified by caustic soda or caustic potash at a low temperature, and the methyl alcohol set free, being volatile, is readily recovered for re use It would appear, however, that the process may also constitute a valuable means of obtaining mono esters for fractionation to produce "tailor made" fats and oils The methyl and ethyl esters of fatty acids are fluid, relatively stable, and noncorrosive, and hence are to be preferred to the free acids, particularly where fractionation must be carried out at an elevated temperature, as by distillation or liquid–liquid extraction

The reverse of the above reaction, in which methyl or other low molecular weight alcohol is displaced from its fatty acid esters by glycerol, to yield triglycerides and free alcohol, is less easily carried out, but may be accomplished by virtue of the greater volatility of the lower alcohols, as compared with glycerol The methyl esters are reacted with glycerol, and sodium hydroxide or other catalyst, at a high temperature with stirring, under reduced pressure The methyl alcohol gradually distills off, leaving the fatty acids combined with the glycerol

(c) *Manufacture of Mono and Diglycerides*

The manufacture of mono and diglycerides represents a special case of interesterification, between fats and an excess of glycerol In the simplest terms, the reaction may be represented as follows



Actually, it is probable that triglycerides react with mono and diglycerides, diglycerides and monoglycerides react with glycerol and with each other, etc In any case, it is not possible to prepare a product consisting substantially of either mono or diglycerides, the commercial products consist of a mixture of the two, with possibly also triglycerides present

Mono and diglycerides are manufactured for industrial use in considerable quantities They serve as intermediates in the manufacture of various

fatty products, including oil modified alkyd resins Also they are efficient oil soluble emulsifying agents, probably their most important use is as an ingredient of the so called superglycerinated shortenings

Reaction between the fat and glycerol is carried out in closed vessels provided with mechanical agitation The vessels are preferably constructed of aluminum, nickel, or stainless steel, as ordinary carbon steel contaminates the product excessively with iron soaps, and yields a dark product Substantially atmospheric pressures are employed, but the fat should be deaerated before it is heated, and the headspace in the vessel should be flooded with hydrogen or other inert gas The reaction temperature is usually between about 425° and 475°F, and the reaction is completed within about one to two hours Any one of a number of alkaline catalysts may be employed, including lime, caustic soda, trisodium phosphate, soda ash, sodium alcoholates, etc Of these caustic soda is probably the most satisfactory The amount of catalyst used amounts usually to about 0 05–0 20% of the weight of the fat

A fat with a molecular weight corresponding to that of triolein will theoretically require 20 8% of its own weight of glycerol for complete conversion to monoglycerides, and 5 2% for conversion to diglycerides A maximum production of mono, rather than diglycerides is desired if the product is to be used as an emulsifier, but in practice it will be found that no advantage accrues from the use of more than about 30% of glycerol Regardless of the excess used an equilibrium appears to be reached after the fat has combined with about 13 5% of its weight of glycerol If it is assumed that triglycerides are substantially absent in the reaction product, this corresponds to a monoglyceride–diglyceride mixture in the ratio of about 70 to 30 (molar)

The extent to which reaction has occurred may be judged by the actual amount of glycerol combined in the product, by a determination of the hydroxyl content, by the increase in molecular weight occasioned by acetylization, or by the effect of the product on the interfacial tension of fat against water Good products made from hydrogenated cottonseed oil will contain about 20–22% of combined glycerol, and after acetylization will have saponification values of 320 to 340 The addition of 4% of the product to cottonseed oil should reduce the interfacial tension of the latter against water at 45°C to 4 to 6 dynes per centimeter as measured by the ring method

If the mono- and diglycerides are to be used in edible products, the soaps formed by the alkaline catalyst must be removed, as they have a very deleterious effect upon the stability of the fat These soaps cannot be decomposed with mineral acids and then washed out of the product in the usual way, for the mono- and diglycerides are strongly surface active, and form very persistent emulsions with water or any aqueous washing liquid

Eckey and Clark[12] have devised a novel method of removing the catalyst without washing The batch is cooled to about 190° to 210°F, and sufficient 85% phosphoric acid is added to decompose the soaps and provide about 50% excess, along with a small quantity of diatomaceous earth or other filter aid The mixture is then stirred under a vacuum for a few minutes, and filtered Dehydration of the mixture occurs and the soaps are decomposed to form free fatty acids and sodium phosphate The sodium phosphate is insoluble in the oil, and hence is removed with the filter aid

If it is desired to remove unreacted glycerol from the product it may be steam deodorized, but deodorization should be conducted at a low temperature and should not be longer than necessary Mono and diglycerides readily lose combined glycerol under deodorization conditions, and revert to triglycerides Deodorization of mono and diglycerides equivalent to the deodorization customarily given edible fats, e g, 2 hours' steaming at 450°F, will cause most of the added glycerol to be driven off, and prove altogether ruinous to the product If the mono and diglycerides are to be incorporated into a shortening, to produce a superglycerinated product, the deodorization method of Richardson and Eckey[13] is recommended, i e, the mono and diglycerides are added to the shortening while the latter is being deodorized but near the end of the deodorization period If the mono and diglycerides are prepared from deodorized fat, they will require very little deodorization to constitute an acceptable ingredient of an edible fat

While the bulk of the glycerol combined during the preparation of mono and diglycerides is readily distilled out during deodorization, the last portions are very difficult to remove, even under the most drastic deodorization conditions Decomposition of the mono and diglycerides is facilitated by the presence of catalysts The experimental results in Table 161 are typical They comprise the results of a series of tests in which hydrogenated cottonseed oil was reacted with 22% of its weight of glycerol and 0 05% of sodium hydroxide, and then steam deodorized at 500°F for various lengths of time, with and without removal of the catalyst

The conventional methods of making mono and diglycerides are described in a series of Canadian patents issued to Edeler and Richardson [14] Mono and diglycerides may also be prepared by the esterification of fatty acids with an excess of glycerol, as described by Christensen [15] Hilditch

[12] E W Eckey and C C Clark (to Procter & Gamble Co), U S Pat 2 065 520 (1936).

[13] A S Richardson and E W Eckey (to Procter & Gamble Co), U S Pat 2 132 437 (1938)

[14] A Edeler and A S Richardson (to Procter & Gamble Co) Canadian Pats 340,803–05 (1934)

[15] C W Christensen (to Armour & Co), U S Pat 2,022,493 (1935)

and Rigg[16] have claimed an improved process wherein fatty acids are reacted with glycerol in a solvent such as phenol Mono and diglycerides may be prepared by the reaction of fat and glycerol without a catalyst, but in this case a very high temperature (above 500°F) and a prolonged reaction time are required

(d) *Rearrangement of Glyceride Structure*

The melting point, consistency, and other physical properties of fats are determined to a considerable extent by the manner in which the fatty acids are grouped to form triglycerides It follows, therefore, that fats or fat mixtures can often be improved for specific uses by merely effecting a rearrangement of their pre existing fatty acid radicals

At present no practicable method is known for controlling such a re arrangement to the extent of producing any desired glyceride configurations However, processes are available which cause a random reshuffling

TABLE 161
EFFECT OF STEAM DEODORIZATION ON THE DECOMPOSITION OF MONO AND DIGLYCERIDES

Sample	Deodorization time hrs	Glycerol content %	Excess glycerol %
Original oil	—	11 25	—
Mono and diglycerides catalyst removed	2	14 85	3 60
	6	13 72	2 47
Mono and diglycerides catalyst not removed	2	11 65	0 40
	4	11 46	0 21
	7	11 30	0 05

of the fatty acids amongst the triglyceride molecules, and these are in some cases useful The oldest rearrangement process disclosed in the patent literature, that of van Loon[17] was apparently designed to produce improved margarine fats Gooding[18] claims a rearrangement process for interesterifying highly hydrogenated mixtures of lauric acid oils and ordinary oils to produce hard butters of relatively low melting point and short plastic range An example is quoted in which 75 parts of completely hydrogenated palm kernel oil and 25 parts of completely hydrogenated palm oil were reacted to yield a product with a Wiley melting point of 104 5°F , a setting point of 33 0°C , and a very short plastic range Before rearrangement, the mixture had a melting point of 122 3°F

[16] T P Hilditch and J G Rigg (to Imperial Chemical Industries), U S Pat 2 073 797 (1937)

[17] C van Loon (to Naamlooze Vennootschap Anton Jurgens Margarinefabrieken), U S Pat 1 873 513 (1932) Dutch Pat 16 703 (1927) See also U S Pat 1,744,596 (1930) and Brit Pat 249 916 (1924)

[18] C M Gooding (to Best Foods, Inc) U S Pat 2 309 949 (1943)

Bailey[19] rearranges the glyceride structure of lard and hydrogenated lard to eliminate the undesirable crystal habits of these fats As mentioned previously (Chapter IX, pages 213–214, and Chapter XI, pages 283–284), lard and hydrogenated lard have a characteristic tendency to form large, coarse crystals The crystals of hydrogenated lard, for example, appear to be about ten times the length of those of vegetable shortenings, mixtures of tallow and cottonseed oil, etc , even if the lard is solidified very rapidly in the Votator or on the chilling roll As a consequence of its peculiar crystal structure, hydrogenated lard has a coarse appearance, and tends to form emulsions which easily break and lose air, in cake mixing operations by the sugar batter method

TABLE 162

COMPARISON OF LARD PRODUCTS BEFORE AND AFTER REARRANGEMENT CONSISTENCY AND PERFORMANCE OF THE FATS IN A STANDARD POUND CAKE TEST[a]

Consistency and performance	Leaf lard		Hydrogenated lard	
	Before rearrangement	After rearrangement	Before rearrangement	After rearrangement
Micropenetrations, mm /10, at				
70°F	62	65	40	53
80°F	80	130	60	125
90°F	140	225	110	285
Pound cake test (air incorporated, %)				
Period 1	62	225	170	265
Period 2	88	268	225	280
Period 3	80	315	212	325
Period 4	75	253	185	248
Loaf volume, cc /lb	850	1495	1265	1410

[a] For a description of the pound cake test, and explanation of the mixing periods and method of calculating the per cent air incorporated in the fat, see Chapter XI, page 284

Rearrangement of hydrogenated lard breaks up the particular glycerides responsible for the formation of coarse crystals, and enables the fat to perform satisfactorily in cake baking Rearrangement of unhydrogenated lard has a similar effect, and also improves the creaming qualities of the fat The data in Table 162 are typical of lard products subjected to re arrangement

(e) *Composition of a Re esterified or Rearranged Fat*

In the case of a fat composed of re esterified fatty acids and glycerol, or a fat whose molecular structure has been rearranged by one of the methods presently to be described, the fatty acids are apparently distributed in a

[19] A E Bailey (to Cudahy Packing Co), U S Pat Applications 319,130 (1940), 478,078 (1943)

truly random manner among the glyceride molecules It follows, therefore, that if the fatty acid composition of such a fat is known the glyceride composition may be determined mathematically Formulas for calculating the composition in terms of glycerides are as follows

Where A, B, C, D, etc are the molar percentages of fatty acids a, b, c d, etc in the fat, the molar percentage of a glyceride containing only one of the fatty acids will be the cube of the molar percentage of the fatty acid, divided by 10 000 For example

$$\text{Per cent glyceride } a\ a\ a = (A\ A\ A)\ 1/10{,}000$$

The molar percentage of a glyceride containing two different fatty acids will be the square of the molar percentage of the fatty acid occurring twice times the molar percentage of the fatty acid occurring once times 3 divided by 10,000 For example

$$\text{Per cent glyceride } a\ a\ b = (A\ A\ B)\ 3/10\ 000$$

The molar percentage of a glyceride containing three different fatty acids will be the product of the molar percentages of the three acids, times 6, divided by 10 000 For example

$$\text{Per cent glyceride } a\ b\ c = (A\ B\ C)\ 6/10{,}000$$

The use of the above formulas will be illustrated by a single example Suppose that re esterified or rearranged fat contains stearic, oleic, and linoleic acids in the following molar proportions

Stearic acid	20%
Oleic acid	30%
Linoleic acid	50%
Total	100%

The molar proportions of the various glycerides will be as follows

Stearic stearic stearic	= (20 20 20) 1/10 000 =	0 8%
Oleic oleic oleic	= (30 30 30) 1/10 000 =	2 7
Linoleic linoleic linoleic	= (50 50 50) 1/10 000 =	12 5
Stearic stearic oleic	= (20 20 30) 3/10 000 =	3 6
Stearic stearic linoleic	= (20 20 50) 3/10 000 =	6 0
Oleic oleic stearic	= (30 30 20) 3/10,000 =	5 4
Oleic oleic linoleic	= (30 30 50) 3/10 000 =	13 5
Linoleic linoleic stearic	= (50 50 20) 3/10 000 =	15 0
Linoleic linoleic oleic	= (50 50 30) 3/10 000 =	22 5
Stearic oleic linoleic	= (20 30 50) 6/10,000 =	18 0
	Total =	100 0%

Present methods for analyzing fats in terms of their component glycerides are too inadequate to permit complete experimental verification of the randomness of fatty acid distribution in re-esterified or rearranged fats However, Bhattacharya and Hilditch[8] have been able to confirm the fact that the fully saturated glyceride content of such a fat conforms to the principle of random distribution These workers have found that the use of

a considerable excess of fatty acids in re esterification does not affect the composition of the product so long as the different fatty acids differ in chain length by no more than two carbon atoms Stearic and palmitic acids, for example, are esterified at about the same rate However, if the fatty acid mixture contains one acid of relatively low molecular weight, such as lauric acid, and the acids are employed in considerable excess over the glycerol, the esterified fat will contain a disproportionately large share of the low molecular weight acid, due to the latter being more readily esterified than the higher molecular weight acids

It has repeatedly been observed by the author that the consistency and melting points of different fats are brought to definite and duplicable values by re esterification or rearrangement, and that these values are independent of the specific method used to bring about rearrangement

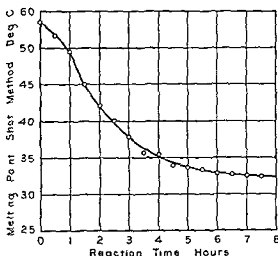


FIG 104 —Rearrangement of a mixture of 15% cottonseed oil stearine and 85% soybean oil at 450°F Catalyst, stannous hydroxide equivalent to 0 39% tin

The effect of rearrangement upon the melting point and consistency of a fat is predictable from the fatty acid composition of the latter A fat such as a blended type shortening, which contains considerable fully saturated glycerides, but no very large proportion of saturated acids, will have its melting point much lowered by rearrangement (Fig 104), due to the tendency of the process to distribute the saturated acids more evenly amongst the glyceride molecules It can be calculated that a rearranged fat must contain 21 5% of saturated fatty acids in order to have as much as 1 0% of fully saturated glycerides On the other hand, fats such as oleo oil, cocoa butter, or cottonseed oil, which contain a considerable amount of saturated acids, but little or no fully saturated glycerides, will have their melting points raised by rearrangement An oleo oil, for example, may contain 45% of saturated acids, but practically no completely satu-

rated glycerides After rearrangement, it will contain approximately 9 1% of these glycerides

(f) Rearrangement with a Metallic Catalyst

The patents of van Loon[17] disclose a method of effecting rearrangement by heating the fat at 200–225°C with a catalyst such as sodium ethylate or stannous hydroxide

A suitable catalyst for the van Loon process may be prepared as follows 45 parts by weight of stannous chloride ($SnCl_2$ $2H_2O$) are dissolved in 3000 parts of water, in which is suspended 40 parts of diatomaceous earth To this is added slowly with stirring 500 parts of water in which have been dissolved 25 grams of sodium carbonate (Na_2CO_3) The precipitate is filtered and washed with cold water The fresh wet filter cake is added directly to the reaction vessel This catalyst loses much of its activity upon drying or prolonged storage

In Figure 104 are shown graphically the results of a test in which there was reacted at 450°F under an atmosphere of hydrogen a fat containing an amount of the above catalyst equivalent to 0 39% tin The fat in this case was a mixture of 15% highly hydrogenated cottonseed oil with soybean oil, the extent of rearrangement being indicated by the decrease in the melting point of the mixture

Certain other metallic hydroxides, including those of lead and cadmium, are also catalysts for the van Loon reaction

(g) Rearrangement with the Aid of Glycerol or Other Alcohols

Another rearrangement process[18-20] employs a small amount of glycerol as a catalyst Actually, the glycerol reacts to form mono or diglycerides, and interchange occurs through the medium of the free hydroxyl groups in these, until a random distribution of the fatty acid radicals is obtained After rearrangement is completed, the added glycerol may be removed by high temperature steam deodorization If desired, preformed mono and diglycerides may of course be used as catalysts, other polyhydric alcohols, such as glycol, mannitol, sorbitol, polyglycerol, etc , may theoretically be employed, although they are generally less desirable for the purpose than glycerol

Rearrangement is greatly assisted by the presence of a small amount of sodium hydroxide or other material capable of catalyzing the formation of mono and diglycerides In practice, relatively large amounts of glycerol, e g , 2% to 5%, and a very high temperature, 500° to 525°F , are required to complete the rearrangement in 6 hours or less, in the absence of an alkaline assisting catalyst If 0 05% of sodium hydroxide is used, the

[20] A E Bailey (to Cudahy Packing Co), U S Pat Applications 316,685, 319,127 319,138, and 319,129 (1940) and 477,255 (1943)

glycerol may be reduced to as little as 0 2% to 0 5% and the temperature may be as low as 450°F

For the rearrangement reaction vessel, aluminum is a very suitable material, although stainless steel and nickel are also satisfactory The vessel must be provided with a means for heating to a high temperature, an efficient agitator, and connections to a vacuum pump The reaction is carried out at atmospheric pressure, but to protect the charge from oxidation, the headspace must be filled with hydrogen or other inert gas

The alkaline catalyst is removed from the finished product with strong phosphoric acid, as described in the manufacture of mono and diglycerides If it is desired to remove the added glycerol very completely, steam deodorization must be carried out before the alkaline catalyst is removed, otherwise deodorization is the final step in the process

The process of Grun,[21] which comprises reaction of the fat with glycerol to form mono and diglycerides, followed by conversion of these to triglycerides by heating with fatty acids, accomplishes the same purpose as the above described rearrangement

[21] A Grün, U S Pat 1,505 560 (1924)

CHAPTER XXII

POLYMERIZATION, ISOMERIZATION, AND RELATED PROCESSES

1. Polymerization of Oils through Heat and Oxidation

Both the theory and practice of the polymerization of drying oils have been treated at some length in Chapter XIII, pages 369–389 Only the mechanics of the process remain to be considered here

A somewhat sharp distinction may be made between polymerization effected largely through the agency of heat, and polymerization in which oxidation plays a prominent role Heat polymerization is considered to produce direct carbon to carbon linkages between the unsaturated acid chains, whereas polymerization accompanied by oxidation presumably occurs to a considerable extent through the establishment of carbon oxygen carbon linkages

Most of the polymerized oil produced at present is utilized in protective coatings For the manufacture of this class of products heat polymerized oils are generally, although by no means always, preferred On the other hand, the linoleum industry, which is the second largest user of polymerized oils, requires a highly oxidized polymer

Formerly, purely heat polymerized oils were not generally available The common practice was to polymerize the oil by heating in an open kettle, with free access to the air hence in the operation the oil invariably underwent considerable oxidation Oils are now often heat treated in a closed vessel under a vacuum or an atmosphere of carbon dioxide, with very little oxidation taking place

The kettles used for heat bodying or polymerizing drying oils vary extremely in capacity, design, and method of operation The cruder installations consist simply of open cylindrical kettles, unstirred, or stirred by hand, and heated by a direct fire The most modern kettles are closed, provided with agitators, and heated by electric resistance heaters, circulated hot mineral oil or the condensation of Dowtherm vapors As in other processes requiring oil to be heated to a high temperature, the Dowtherm system of heating is particularly desirable, because of its simplicity, economy, and ease of control (see pages 540–542, Chapter XVII)

In order to avoid oxidation during the course of polymerization, where this is desired, connections are provided for blanketing the oil with carbon dioxide or flue gas, or the batch may be kept under a vacuum of about 20–30 mm In the event that an inert gas is used, it may be continuously

bubbled through the oil mass, or merely flooded over the surface of the batch In some cases where an inert gas is used, a partial vacuum is also maintained on the kettle As compared with other processing vessels used in the oil and fat industry, the kettles are usually small Their size is limited by difficulties in providing sufficient heat transfer surface for reasonably rapid heating In order to provide free circulation of the relatively viscous oil in the kettle, heating coils are avoided, hence the heat must be transferred entirely through the kettle walls The largest kettles have a capacity of 500 to 1000 gallons, although kettles of 100 to 250 gallons capacity are more common They are preferably constructed of metals such as stainless steel, or nickel clad steel, to avoid contaminating and darkening the oil with iron soaps In the best equipment, temperature control is entirely automatic

For the best control of the bodying operation it is desirable to have some means of quickly reducing the temperature of the batch, and thus arresting the reaction, when the desired degree of polymerization is attained If the kettle is heated by Dowtherm vapors, the batch may be cooled by the circulation of cold Dowtherm liquid through the heating jacket Electrically heated kettles are often provided with an auxiliary cooling tank, into which the hot batch may be dropped Tung and oiticica oils polymerize very rapidly in the latter stages of bodying, hence there is much danger of gel formation in the production of heavily bodied products from these oils, unless the heating is very accurately controlled In the polymerization of such oils it may be necessary to check the reaction by adding a portion of cold oil Small batches of oil can of course be cooled more quickly than large batches

The degree to which an oil is polymerized is measured in terms of its viscosity, hence the reaction may be followed by periodically withdrawing samples and checking the viscosity As polymerization proceeds, the change of viscosity in unit time becomes progressively greater, a plot of bodying time against kinematic viscosity yielding a curve of an approximately exponential form If the temperature of the batch is maintained constant during the period of observation, and the time is plotted against the logarithm of the viscosity, there will usually be obtained either a substantially straight line, or a series of two or more straight lines (Figs 105 and 106)

Where the time–viscosity curve so plotted consists of more than one straight line, each linear portion may be presumed to represent some definite degree of molecular aggregation Shuey[1] has observed that if the viscosity of heat bodied tung oil is determined at the temperature of the kettle, rather than upon cooled samples, a curve is obtained with three well

[1] R C Shuey, *Ind Eng Chem*, **32**, 921–930 (1940) See also J J Mattiello, editor, *Protective and Decorative Coatings*, Vol III, Wiley, New York, 1943, pp 125–129

defined linear phases The point corresponding to the end of the first phase is almost exactly that at which the oil begins to become insoluble in acetone, whereas the point corresponding to the end of the second phase is that at which the oil begins to become insoluble in mineral spirits At 450°F the viscosities represented by the "acetone" and "mineral spirits" points are respectively about 10 and 25 centipoises

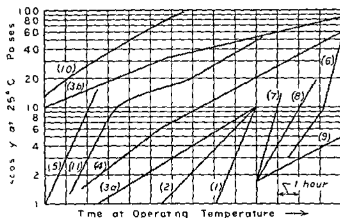


FIG 105 —Bodying time *vs* viscosity in the heat bodying of various drying oils
(1) Linseed oil, commercial, 625°F [2]
(2) Linseed oil, commercial, 575°F [3]
(3) Linseed oil, commercial, 550°F [3]
(4) Linseed oil, commercial, 565°F [3]
(5) Soybean oil, laboratory, 600°F [4]
(6) Dehydrated castor oil, commercial, 550°F [5]
(7) Dehydrated castor oil, laboratory, 590°F [6]
(8) Dehydrated castor oil, laboratory, 560°F [6]
(9) Dehydrated castor oil, laboratory, 500°F [6]
(10) Sardine oil, I V 201, clear 8 hrs at 32°F, commercial, 555°F [7]
(11) Menhaden oil, I V 179 2, *commercial*, 565°F [8]

Viscosity-time curves for a number of drying oils bodied at different temperatures are recorded in Figures 105 and 106 The rate of bodying increases quite rapidly with the temperature, doubling for each increment

[2] B P Caldwell and J Mattiello *Ind Eng Chem*, 24, 158–162 (1932)
[3] J Mattiello and L T Work, *Natl Paint, Varnish Lacquer Assoc Circ No* 502 (1936)
[4] A J Lewis, *private communication*, 1944
[5] J F Gerkens and V A Kildare in *Protective and Decorative Coatings* Edited by J J Mattiello, Vol III Wiley, New York, 1943, pp 82–85
[6] J D Von Mikusch, *Ind Eng Chem*, 32, 1061–1069 (1940)
[7] Los Angeles Production Club, *Natl Paint, Varnish Lacquer Assoc Circ No* 546, 263 271 (1937)
[8] L T Work, C Swan, A Wasmuth, and J Mattiello, *Ind Eng Chem*, 28, 1022–1024 (1936)

of about 25°F The doubling interval appears to be very nearly the same for oils of quite different compositions Von Mikusch[6] calculated it to be about 24°F for linseed oil in the range of 550–625°F, and about 27°F for dehydrated castor oil in the range 500–590°F

The curves of Figures 105 and 106 give an indication of the actual times required to heat body different oils at different temperatures In general, the atmosphere in which the operation is carried out does not appear to have any large effect upon the bodying rate, nearly equivalent times being required for bodying in air, under carbon dioxide, and under a vacuum In practice, a considerable time will of course be required to bring the batch to operating temperature Some degree of bodying will occur during the heating period, and allowance must be made for this in estimating the

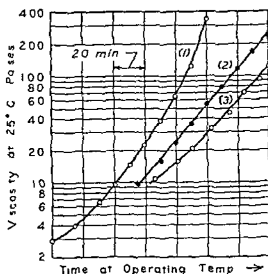


FIG 106 —Bodying time *vs* viscosity in the heat bodying of tung and oiticica oils (1) tung oil, 450°F in air, (2) oiticica oil, 450°F, in air, (3) oiticica oil 450°F, in carbon dioxide [9]

total time for the operation Methods for calculating the heating equivalent of the warm up period, in terms of time at the top temperature, have been given by Turkington, Shuey, and Schechter,[10] and Von Mikusch[6] The Von Mikusch formula is particularly useful

$$H = 1.44\, D/c$$

where H = heating equivalent in minutes, D = doubling interval (see above), and c = heating rate in degrees F per minute This formula

[9] S O Sorenson C J Schumann, J H Schumann, and J Mattiello, *Ind Eng Chem*, 30, 211–215 (1938)

[10] V H Turkington R C Shuey, and L Schechter *Ind Eng Chem*, 30, 984–990 (1938)

assumes a constant heating rate and a constant doubling interval for the oil It is applicable to cooling, as well as heating, that is

$$C = 1.44\ D/c'$$

where C = cooling equivalent and c' = cooling rate

In commercial practice, linseed oil is usually bodied at some temperature between about 560° and 625°F Soybean oil bodies more slowly than linseed oil, and hence requires a high temperature, *e g*, 600° to 625°F Dehydrated castor oil is bodied at lower average temperatures than linseed oil, *e g*, at about 550°F Fish oils are also bodied at about this temperature Polymerization is so rapid in tung and oiticica oils that these are not generally bodied at temperatures above about 450°F

In selecting the temperature at which polymerization is to be conducted, a balance must be struck between the desirability of operating at a high temperature, to decrease heating costs and increase the daily capacity of the kettles, and the desirability of operating at a low temperature, to avoid excessive losses through volatilization and to obtain a better oil Oils bodied at a relatively low temperature are lighter in color and lower in acidity than oils bodied at a high temperature, and are generally considered to yield more durable paints and varnishes They also are less inclined to form products which liver in the package [3]

When bodied in contact with the air linseed oil darkens considerably and also increases progressively in free fatty acid content as bodying is continued In large scale tests in which linseed oil was bodied in air at 535°, 575°, and 600°F, Mattiello and Work[3] found that the acid numbers of the oils at a viscosity of 60 poises were, respectively, about 6, 10, and 14 In corresponding tests conducted under vacuum the acid number did not increase progressively, and was in no case greater than about 2 in the finished product The oil also darkened less under vacuum than in the air However, linseed oil developed a higher acidity when bodied under carbon dioxide than when bodied in air Vacuum bodied oils are said to have practically no tendency to liver [3]

Tung oil becomes lighter during polymerization and does not increase in acidity even when exposed to the air during the operation The tendency of oiticica oil to increase in acidity during bodying is but slight Sardine oil, or other fish oils exhibit a somewhat peculiar behavior in heat bodying If sardine oil, whether winterized or unwinterized, is bodied to a viscosity greater than about 10 poises, it is inclined to form a so called polymer cloud, and precipitate solid gel particles [7] This characteristic of the oil may be presumed to be due to the peculiar glyceride composition of marine oils, or in other words, to the fact that these oils contain very highly unsaturated and reactive glycerides mixed with a large proportion of other glycerides which are relatively unreactive Polymerization of

such a mixture would naturally be expected to proceed unevenly[11] For the production from fish oils of heavy bodied oils not subject to clouding, it is recommended[7] that the oil be first heat bodied to a viscosity of about 9 poises, and then further increased in viscosity by air blowing A temperature of 535°F was suggested as optimum for bodying fish oils At this temperature the oil was observed to increase in molecular weight more rapidly than at 555°F, and to develop but little acidity

A considerable loss of oil is invariably incurred during heat bodying, through decomposition and volatilization of the decomposition products The actual loss in any case will depend upon the temperature of operation, the nature of the oil, the degree to which it is bodied, and whether the volatile products are continuously removed or partially condensed and returned to the kettle Losses as high as 10% or higher are often recorded in the manufacture of heavy bodied products from oils which polymerize with relative slowness

Relatively simple equipment is required for the manufacture of blown oils, which are generally processed at a temperature under about 250°F The operation consists simply of blowing a vigorous current of air through the heated oil until the desired viscosity is attained If the operation is prolonged, the reaction may become sufficiently exothermic to require the batch to be cooled, in order to maintain the proper temperature Oils are blown to various degrees of polymerization, according to their particular uses In some cases, particularly where it is desired to reduce the time required for heat bodying, or where a surface active oil is desired, drying oils are first slightly polymerized by blowing, and then heat polymerized For some purposes, a certain degree of oxidation is desired during heat bodying The practice of "top firing," or heating in an open kettle while burning off the volatile products of reaction is still followed in polymerizing oils for certain varieties of printing inks

The solid "linoxyn" used in the manufacture of linoleum must be almost entirely oxygen polymerized, at a temperature not in excess of about 120°F The special methods used for making this product are described in Chapter XIV

A number of special methods have been patented for the rapid and continuous polymerization of drying oils These are discussed on page 389

[11] *In this connection see also* H N Brocklesby, *The Chemistry and Technology of Marine Animal Oils* Fisheries Research Board of Canada Ottawa 1941 pp 127–128 Brocklesby considers that the 'polymer cloud" is composed at least in part of precipitated glycerides of a high degree of unsaturation which become insoluble in the polymerized oil He points out that there may well be rearrangement of the glycerides in the oil during bodying to produce fully saturated glycerides (see Chapter XXI, pages 681–686)

2. Polymerization with Assistance of Added Substances

There are a number of substances which promote polymerization when added to unsaturated oils Some of these are effective in small amounts, and appear to act catalytically Others very definitely enter into permanent chemical combination with the oil, and may be incorporated into the oil in considerable quantity

The leading example of a polymerizing agent which reacts chemically with the oil, to establish cross linkages between unsaturated fatty acid chains, is furnished by sulfur and certain of its compounds The use of these in the manufacture of factice has been outlined on pages 421–423, Chapter XIV Sulfur compounds have also been patented as catalytic polymerization agents The use of sulfur dioxide is claimed by Vlodrop and Waterman [12] However, sulfur inhibits the drying of oils, and may be used to prevent gelation in the heat bodying of tung oil Gardner[13] employs sulfur or sulfur-containing compounds in the bodying of tung oil, to prevent gelation, and removes the sulfur at the conclusion of the operation by reaction with copper Harper[14] uses selenium for the same purpose Parkin[15] has patented the use of diaryl and dialkyl disulfides

Hydrogen chloride is mentioned by a number of writers as a catalytic agent for the heat bodying of oils Long and Ball[16] have patented a class of resinous drying oil products in which chlorine is combined Various metallic chlorides are used by Stoddard, Geiger, and Burgess[17] for polymerizing drying oils Boron fluoride has received particular attention as an assistant for the polymerization of fatty oils to be used with petroleum products in compounding lubricants [18] Rheineck and Crecelius[19] claim silicotungstic acid and other tungstic acids as catalytic agents for oil bodying

A number of metallic catalysts for polymerization have been patented, in addition to the metallic dryers commonly used in boiled oils A novel method of incorporating metallic dryers such as nickel, cobalt, iron, etc, in the form of carbonyls, is revealed by Ambros, *et al* [20]

Among the patents embodying the use of organic accelerators for the

[12] H I Waterman and C van Vlodrop (to Imperial Chemical Industries, Ltd), U S Pat 2,188,273 (1940)

[13] H A Gardner, U S Pat 1 986,571 (1935)

[14] W J Harper, U S Pat 2,152 642 (1939)

[15] F P Parkin (to Minnesota Linseed Oil Paint Co), U S Pat 2 263 887 (1941)

[16] J S Long and G L Ball U S Pat 2 044,007 (1936)

[17] W B Stoddard, T H Geiger, and L M Burgess U S Pat 1,924 524 (1933)

[18] E Eichwald, U S Pat 2,160 572 (1939), J M Whitely and L B Turner (to Standard Oil Development Co), U S Pat 2,260,417 (1941)

[19] A E Rheineck and S B Crecelius (to Devoe & Reynolds Co), U S Pat 2 345 358 (1944)

[20] O Ambros, H Reindel, J Eisele, and J Stoehrel, U S Pat 1,891,203 (1932)

heat bodying of oils there may be mentioned those of Schwarcman[21, 22] and Sorensen and Konen [23] Schwarcman claims the use of phenanthrene like compounds, including chrysene, retene, and picene, which have been oxidized sufficiently to contain ketone and hydroxyl groups,[21] and also polycyclic aromatic compounds containing one carboxyl group and at least two hydroxyl groups, as for example, diphenolcarboxyl anthracene [22] The promotive agents of Sorensen and Konen are compounds *containing at least three* aromatic rings, including phenanthrene, anthracene, anthroquinone, and their derivatives

3. Alkali Isomerization of Drying Oils

The alkali isomerization process for the production of conjugated acid oils from ordinary drying oils grew out of the observation by biochemical workers[24] that there is a tendency for double bonds to undergo a shift in position in the alcoholic saponification of drying oils The first reported method[25] for producing extensive conjugation in a short time specified treatment with alkali in an alcohol or other high boiling organic solvent However, it has subsequently been shown that reaction in an aqueous alkali solution is equally effective, if the operation is carried out at a sufficiently high temperature, and of course under a correspondingly high pressure Aqueous alkali isomerization is employed in the commercial manufacture of the isomerized oils

The fundamentals of aqueous alkali isomerization are discussed in an article by Bradley and Richardson [26] These workers found that it was readily possible to produce soybean oil and linseed oil products containing from 30–50% of conjugated fatty acids The principal factor affecting the rate of reaction and composition of the reaction product was the temperature, the alkalinity of the reaction mixture and the proportion of water present were found to be only minor factors The data of the above authors relative to the effect of temperature are shown in Table 163 There is an optimum reaction time, beyond which there is a decrease in conjugation of the fatty acids

In commercial practice, soybean oil and linseed oil are said to be first split, and the free acids are subjected to isomerization by caustic soda The isomerized acids are recovered from their sodium soaps by acidulating

[21] A Schwarcman (to Spencer Kellogg & Sons) U S Pat 2 207,686 (1940)
[22] A Schwarcman (to Spencer Kellogg & Sons), U S Pat 2 230 470 (1941)
[23] S O Sorensen and J C Konen (to Archer Daniels Midland Co), U S Pat 2 213 935 (1940)
[24] W J Dann and T Moore, *Biochem J* 27, 1166–1169 (1933) W J Dann R G Booth, J Golding and S K Kon, *ibid*, 29, 138–146 (1935) T Moore *ibid* 31, 138–154 (1937)
[25] G O Burr (to Regents of the University of Minn), U S Pat 2 242 230 (1941)
[26] T F Bradley and D Richardson *Ind Eng Chem* 34 237–242 (1942)

the latter, and are then re esterified with glycerol The isomerization reaction is said to be carried out in a continuous apparatus, details relative to the proportions of alkali, water and fatty acids, the reaction time, and the operating temperature are not available

It has been found that the amount of conjugation produced during alkali isomerization is not an absolute measure of the drying properties of the isomerized oil, since isomers of a high degree of conjugation but relatively

TABLE 163

EFFECT OF THE REACTION TEMPERATURE ON THE ALKALI ISOMERIZATION OF SOYBEAN AND LINSEED OILS[a]

(All runs made with 500 parts by weight of oil, 75 parts of sodium hydroxide, and 500 parts of water)

Time at max temp hrs	Max temp °C	n_{25}^{D}	Analysis of recovered ac ds Per cent conjugated acids 2 double bonds	Analysis of recovered ac ds Per cent conjugated acids 3 double bonds
		A SOYBEAN OIL		
48	165	1 4690	17 8	1 66
48	185	1 4713	39 2	1 75
36	185	1 4711	37 5	1 90
24	185	1 4692	32 5	2 08
18	185	1 4689	26 8	2 13
4	225	1 4708	35 1	1 45
3 5	225	1 4701	39 8	1 55
2 5	225	1 4676	20 2	1 33
0 5	250	1 4720	43 8	2 2
5 min	280	1 4714	40 2	1 3
		B LINSEED OIL		
48	165	1 4788	26 9	5 1
24	165	1 4761	22 6	8 5
21 5	185	1 4807	32 0	9 7
18	185	1 4802	31 1	11 3
12	185	1 4794	27 6	11 1
4	185	1 4745	17 8	5 2
1 5	185	1 4724	13 0	2 5
3	225	1 4803	41 0	8 2
4	225	1 4802	33 6	5 6
0 5	250	1 4805	35 2	9 7

[a] T F Bradley and D Richardson *Ind Eng Chem* 34, 237 242 (1942)

poor drying properties may be produced A high reaction temperature is said to be particularly favorable to the production of slow drying isomers In the case of isomerized linolenic acid, one of the latter isomers appears to be 10 11, 12 13, 14 15 octadecatrienoic acid[27] or "pseudo eleostearic" acid, which dries at but one fourth the rate of natural 9 10, 11 12, 13 14 eleostearic acid[28]

[27] J P Kass and G O Burr *J Am Chem Soc*, 61, 3292–3294 (1939)

[28] J E Meyers J P Kass and G O Burr, *Oil & Soap* 18, 107–109 (1941)

4 Other Catalytic Isomerization Methods for Drying Oils

There is a tendency for the double bonds of unsaturated fatty acids to shift to conjugated positions under the catalytic influence of a wide variety of finely divided solid materials Even in the ordinary bleaching of drying oils with fuller's earth at 100–120°C , measurable conjugation takes place [29]

It has been observed that the heating of linseed oil or its methyl esters in the presence of a nickel hydrogenation catalyst at 200° to 400°C for 8 to 12 hours will produce about 10% of conjugated acids [30] Turk and Feldman[31] used Florida fuller's earth, bentonite, kieselguhr, silica gel and other siliceous materials as isomerization catalysts, carrying out the reaction at 250–300°C , for 3–4 hours with 1–5% of catalyst Substantial changes were noted in the refractive indices of menhaden oil, linseed oil, and linseed oil fatty acids treated under these conditions, indicating the possible formation of conjugated acids to the extent of 25–50% of the total fatty acids

So far none of these catalytic methods has proved effective enough to warrant its commercial development for the production of conjugated acid oils However, they present interesting possibilities, inasmuch as their successful application would eliminate the fat splitting and re esterification required in the alkali isomerization process

5 Dehydration of Castor Oil

As mentioned previously (page 390), the dehydration of castor oil involves the removal of the hydroxyl group from ricinoleic acid, together with an adjacent hydrogen atom, to yield both 9 10 11 12 and 9 10, 12 13 octadecadienoic acids In the original process developed by Scheiber,[32] the separated fatty acids of castor oil were dehydrated, and thereafter re esterified with glycerol However, most of the oil made at present is produced by direct dehydration of the oil

The effective catalysts for dehydration include acid derivatives of sulfuric and phosphoric acids, oxides of tungsten and molybdenum, and certain natural clays Sodium acid sulfate is a particularly suitable catalyst, this and other acid compounds of nonoxidizing mineral acids containing oxygen have been patented by Ufer [33] Schwarcman[34] claims the use of kieselguhr or other siliceous material carrying a small amount of free sulfuric acid The use of Japanese acid earth is mentioned by Yamada [35] Rheineck and Crecelius[19] have patented silicotungstic, phos

[29] J H Mitchell and H R Kraybill, *J Am Chem Soc* , 64, 988–994 (1942)

[30] See *Am Ink Maker*, 20, No 5, 41 (1942)

[31] A Turk and J Feldman *Paint Oil & Chem Rev* 106, No 13 10–11 (1943)

[32] J Scheiber, Ger Pat 513 309 (1930), Brit Pat 316 538 (1928), U S Pat 1,912 778 (1934)

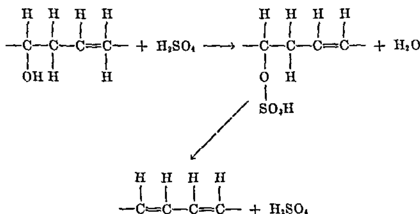
[33] H Ufer (to I G Farbenindustrie), U S Pat 1,892 258 (1932)

[34] A Schwarcman (to Spencer Kellogg & Sons), U S Pat 2 140 271 (1938)

[35] T Yamada, *J Soc Chem Ind Japan, Suppl Bind* , 38, 120–123 (1935)

photungstic, borotungstic, and molybdophosphotungstic acids as dehydration catalysts

It is considered by Forbes and Neville,[36] who have made an extensive investigation of different catalysts, that the acidic catalysts probably function according to the following mechanism



The reaction is carried out in closed kettles preferably constructed of stainless steel, which are provided with agitators and some means of producing a reasonably low vacuum The temperature employed is in the range of about 450° to 475°F , hence a special high temperature heating system must be provided The operation is conducted under reduced pressure, to facilitate removal of the evolved water

Ordinarily less than one per cent of catalyst is used, in the form of a powder It is important for the catalyst to present a large surface, as the system is heterogeneous, at the conclusion of the reaction the catalyst is filtered out of the cooled oil

It has been shown by Priest and Von Mikusch[37] that ordinary 9 10, 12.13 linoleic or octadecadienoic acid is produced by dehydration in considerably greater quantity than the more desirable 9 10, 11 12 conjugated octadecadienoic acid (page 392) It is claimed that the oil, Dienol, produced by the Swiss Munzel process[38] contains only 9 10, 11 12 acid, but this claim has not been confirmed by workers in the United States [37]

6 Oxidation-Dehydration and Halogenation-Dehydrohalogenation Methods for Improvement of Drying Oils

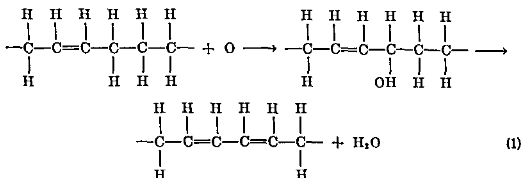
New double bonds may be introduced into unsaturated fatty acids or glycerides in conjugated positions by oxidation followed by dehydration, or halogenation followed by the removal of hydrogen halide The following

[36] W C Forbes and H A Neville *Ind Eng Chem* , 32, 555–558 (1940)

[37] G W Priest and J P Von Mikusch *Ind Eng Chem* , 32, 1314–1319 (1940)

[38] See F Münzel, Swiss Pat 193,931 (1938) Also A V Blom in *Varnish Making*, Chemical Pub Co , New York, 1940, pp 31–39

simplified equations will serve to show the essential reactions involved:



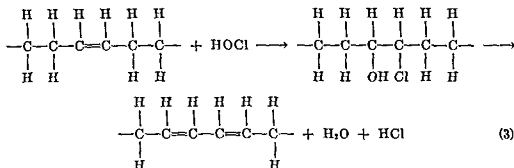
$$-CH_2-CH_2-CH{=}CH-CH_2-CH_2- + Cl_2 \longrightarrow -CH_2-CH_2-CHCl-CHCl-CH_2-CH_2-$$

$$-CH_2-CH_2-CHCl-CHCl-CH_2-CH_2- \longrightarrow -CH_2-CH{=}CH-CH{=}CH-CH_2- + 2\,HCl \qquad (2a)$$

$$-CH_2-CH_2-CHCl-CHCl-CH_2-CH_2- \xrightarrow{(+\,2\,NaOH)} -CH_2-CH_2-CH(OH)-CH(OH)-CH_2-CH_2- + 2\,NaCl$$

$$\downarrow$$

$$-CH_2-CH{=}CH-CH{=}CH-CH_2- + 2\,H_2O \qquad (2b)$$



Improvement in the drying properties of cottonseed and soybean oils following chlorination and dehydrochlorination was reported by Gardner and Bielouss[39] as early as 1922 Recently, treatment of a specially dehydrated castor oil with hypochlorous acid, followed by dehydration and dehydrochlorination (see reaction 3 above), is said to have been used in Switzerland[40] for the commercial production of a synthetic oil, Trienol, containing triply conjugated acids This product is said to polymerize and dry even more rapidly than natural tung oil Details of the process have not been made public, and samples of the product have not been available for examination by chemists in the United States

A patent has been issued to Boone[41] covering a process in which soybean oil is blown with air to introduce hydroxyl groups, and then dehydrated, to produce conjugated double bonds Turk, Dawson, and Soloway[42] have reported the oxidation of oils with selenium dioxide to introduce hydroxyl groups Linseed oil with a diene value of 24 8 and cottonseed oil with a diene value of 17 9 were produced by oxidizing the respective oils, and then dehydrating the oxidized products

Actually, treatment of oils by the methods outlined is not nearly as simple as indicated by the equations, due to the tendency of the materials to react incompletely, or to undergo side reactions Hence at present *none of these methods can be said to have much commercial importance*, although it seems entirely possible that they may in the future, after necessary investigation and refinement

[39] H A Gardner and E Bielouss *J Ind Eng Chem* 14, 619–621 (1922)

[40] See A V Blom in *Varnish Making* Chemical Pub Co, New York, 1940, pp 31–39

[41] P D Boone, U S Pat 2,308,152 (1943)

[42] A Turk, J W Dawson, and S Soloway, *Am Paint J*, 28, No 9, 9, 16, 18, 20 (1943)

CHAPTER XXIII

SOLIDIFICATION, HOMOGENIZATION, AND EMULSIFICATION

1. Introduction

The processes of solidification, homogenization, and emulsification are classified together because they have a common object, as applied to fatty materials The purpose of each is to produce a two phase system, with a high degree of interdispersion of the two phases In the case of solidification, the two phases are respectively the solid and liquid forms of a fat or similar material In the case of emulsification, the two phases are a liquid fat, and water or an aqueous solution The term "homogenization" is applied to treatment designed to produce a further degree of dispersion in a preformed system comprising either solid and liquid fats or fatty and aqueous phases

All fat products which are solidified in the course of their manufacture are actually *plastic solids* except at extremely low temperatures, i e, they consist of an intimate mixture of liquid and very small solid particles The liquid is retained in the framework of solids by capillarity, and the tendency of the solid particles to interlock and cohere gives the material the resistance to limited deforming stresses which is characteristic of plastic systems Obviously the plastic properties of such a material are very largely dependent upon such factors as the relative proportions of solids and liquids, the size and size distribution of the solid particles, the shape of the particles, and their rigidity and degree of mutual attraction As some of these factors are influenced by the manner in which solidification is conducted, some care is required in this operation to obtain desirable properties in the solidified product

The technical solidification of fats, soaps, etc is complicated by the fact that these materials are polymorphic, i e, they are capable of existing in different crystal modifications, according to the conditions under which they are solidified Different solid modifications of the same material are different in melting point and other physical characteristics hence polymorphism alone may account for wide variations in the properties of a single plastic product solidified by different methods

The consistency of an emulsion, as well as its stability, depends to a considerable degree upon the extent to which the discontinuous liquid phase is dispersed

2 Solidification and Homogenization of Plastic Products

(a) *Solidification of Lard and Shortenings*

The characteristic structure of commercially solidified lard and shortenings has been shown in Figure 11, page 208 These fats consist of a mass of small needlelike crystals enclosing liquid oil The crystals of lard (and hydrogenated lard) are invariably much larger than those of shortenings, but appear to be of the same shape In the solidification of these fats the finest possible crystal structure is desired, to render the product smooth in appearance and firm in consistency, hence the crystals are formed by chilling the fat very rapidly It is also customary to whip into the fat about 5–20% of its own volume of air, in the form of very small bubbles, most of which are about 10–50 microns in diameter These bubbles are permanently retained by the plastic fat, and serve to give it a white and opaque, rather than a translucent appearance

The oldest apparatus for the solidification of lard and shortenings is the chilling roll, which is similar in both appearance and operation to the roll described previously for the solidification of soap flakes It consists of a large, hollow iron cylinder with a surface machined and ground smooth to true cylindrical form A roll of common size is 4 feet in diameter and 9 feet long, and has a capacity in the neighborhood of 10,000 pounds per hour

The roll is internally refrigerated by the direct expansion of ammonia or other refrigerant, or in some cases by the circulation of cold brine Turning slowly on its longitudinal and horizontal axis, the roll picks up on its surface a thin coating of the molten fat from a trough formed by a wooden frame bearing against the surface and running its full length The trough is supplied by lines from the storage tanks of liquefied fat The temperature of the fat supplied to the roll is somewhat variable, but is in no case very far above the solidification point of the fat In some installations the thickness of the fat coating depends simply upon the viscosity of the molten fat and the speed of the roll In others, an adjustable blade is set close to the roll just above the trough, to scrape off and return to the trough any fat in excess of a definite film thickness

The coating of fat picked up from the trough is carried up over the roll, and having solidified, is taken off by a scraper blade bearing against the roll near the bottom of the side opposite the feed trough The solidified fat, in the form of a thin, translucent, plastic sheet, drops into a "picker box," which consists of a trough bearing a screw conveyor The flights of the conveyor are interspersed with blades which, revolving in the partially filled trough, beat air into the fat The amount of air incorporated is somewhat roughly controlled by varying the amount of fat maintained in

the picker box The temperature of the fat from the roll will vary according to the nature of the fat and the particular method of operating the roll, but will ordinarily be in the neighborhood of about 65° to 70°F The temperature is inclined to rise somewhat in the picker box and in the lines from the picker box, since there is delayed crystallization, with consequent evolution of heat, for some time after the fat is first chilled

From the picker box the fat is fed to a high pressure steam pump which raises the pressure on the lines leading to the filling machine to about 300 to 500 pounds per square inch The fat entering the high pressure system is by no means thoroughly homogenized, and if it is filled at once it will be lacking in smoothness and whiteness, and contain many small, translucent lumps devoid of air Homogenization is accomplished by forcing the fat, under this high pressure, through various devices set in the lines to the fillers These may consist of orifices, slots, screens, valves, etc, but all represent some form of constriction in the line, which applies to the moving material intense shearing forces, and thus breaks up any aggregates of material *In some systems more than one pump is employed to enable* homogenization to be carried out in more stages than is possible with a single pump

After the final stage of homogenization, the product is discharged directly into packages, automatic filling machines being usually used for the smaller packages, while the larger ones are filled by hand

The roll system of solidification, while simple, and requiring the use of relatively inexpensive equipment, is unsatisfactory in some respects The refrigerated surface of the roll is exposed to the atmosphere, and this causes some loss of refrigeration Any moisture in the atmosphere is free to condense on the surface of the roll, and thence be transferred to the solidified fat In humid weather this may be a source of considerable annoyance Probably the greatest disadvantage of the chill roll, however, is the difficulty of controlling it to obtain a uniform product Particular difficulty is experienced in maintaining a constant incorporation of air into the fat This not only makes the product variable in appearance, but also occasions difficulty in filling the packages to a definite weight, since all automatic package filling equipment operates on a volumetric basis

The disadvantages of chill rolls mentioned above are avoided in the newer "Votator" system, which has replaced the roll system altogether in a great many plants In the Votator, solidification takes place in small, externally refrigerated cylinders through which the fat is continuously pumped These are equipped with sharp, fast revolving scraper blades, which are caused to bear lightly against the cylinder walls by centrifugal force and the resistance to rotation offered by the fat Their continual scraping action prevents the formation of a stagnant film on the heat

transfer surfaces, and results in an extremely high rate of heat transfer, so that the units may be built very compactly[1] Thus a Votator handling 10,000 pounds of shortening an hour requires but 12 square feet of heat transfer surface (three 4 inch tubes each 46 inches long) as compared with about 113 square feet on a chill roll of like capacity As indicated in Figure 108, the shaft carrying the scraper blades is large in diameter, so the fat must pass through a very narrow (about $\frac{1}{2}$ inch) annular space between the shaft and the cylinder walls The latter are cooled by the direct expansion of ammonia, with which their jackets are flooded, under 15 pounds of pressure

The following describes the complete sequence of operations in the solidification of lard or shortening through the Votator The melted fat is fed from storage tanks to a small positive displacement rotary pump, which maintains a pressure of about 300 pounds per square inch on the chilling cylinders and other parts of the system The output of the pump may be regulated by means of a by pass from the discharge to the suction Air to be incorporated into the product is metered into the suction of the pump through a flowmeter or other suitable device If desired, nitrogen or other inert gas can of course be substituted for air A pressure regulating valve is installed in the discharge line from the pump, so that a constant pressure is maintained on further parts of the system

A water to oil heat exchanger beyond the regulating valve cools the fat to a temperature slightly above its solidification point, e g, to 110° to 120°F The cooled fat is then passed through three vertical chilling chambers, or "A" units arranged in series In these chambers its temperature is reduced to about 60° to 70°F Chilling is so rapid that the fat leaves the "A" units in a more or less fluid condition However, the nuclei for the formation of very small crystals have been established and the fat is sufficiently supercooled to readily solidify in other unrefrigerated cylinders provided specifically for this purpose These cylinders, termed "B" units, are two in number, and are placed in series directly after the "A" units They are larger than the "A" units, and are provided with beaters which maintain the contents in a moderate degree of agitation It is in the "B" units that solidification is largely completed, with the temperature of the fat rising several degrees, e g, to 75° to 85°F, in the process, due to heat of crystallization If the product is filled into containers while it is supercooled, and allowed to crystallize therein in a static condition, it will be excessively hard, possibly due to the crystals actually growing together and forming a continuous lattice

From the "B" unit the product passes through a homogenizing valve,

[1] For a discussion of heat transfer in the Votator, see H G Houlton, *Ind Eng Chem*, 36, 522-528 (1944)

and thence to another high pressure rotary pump From this point, handling of the material is not different from that described above in connection with the chill roll, except that a single extrusion valve at the filler will provide sufficient homogenization to yield a desirably smooth product

The three cylinder Votator described above has a rated capacity of 9000 to 11,000 pounds of lard or shortening per hour It is operated by one 15 and two 10 horsepower electric motors, and requires 30 tons of refrigeration, at 15 pounds suction pressure (ammonia) A smaller single cylinder machine is also manufactured, with a capacity of 3000 to 4000 pounds per hour

Although the crystallization of a shortening may in most cases be considered substantially complete by the time the shortening is packaged there are certain modifications in structure which normally take place thereafter The fat issuing from the filling nozzles is quite fluid, and it is usually some little time before the fat in the container assumes its final consistency The final process of "setting" may consist in part of simple delayed crystallization, or the delayed establishment of cohesive forces between crystals, but it seems probable that at least in some cases polymorphic transformations are involved Obviously the very rapid chilling occurring on the roll, and more particularly in the Votator, constitutes an ideal condition for the production of unstable, low melting crystal forms Blended type shortenings containing a highly hydrogenated fat are known to be subject to polymorphism, and these are particularly liable to behave peculiarly after filling Shortening of this type, when brought out of the Votator at a relatively low temperature and thereafter stored at temperatures of 45° to 55°F, has been observed to remain semi fluid for weeks or months The same shortening becomes firm, however if held at more elevated temperatures, e g, at 80° to 90°F Blended shortening is very little inclined to fail to set up if it is discharged from the Votator at a relatively high temperature, i e, at 85° to 90°F, regardless of the temperature at which it is subsequently stored

All shortening is inclined to be abnormally hard and to fail to cream well (see page 282), if it is not subjected to a period of tempering at about 80°F or above after filling Shortening which has been tempered may thereafter be held at a low temperature without harm Under certain conditions, and at certain seasons of the year, the shortening will naturally experience a temperature of at least 80° before it is consumed, but shortening which is made in the winter, or placed directly under refrigeration immediately after filling may well reach the consumer in poor condition Shortening plants are usually provided with special tempering rooms, in which all newly filled products are held for a period of about 48 hours at about 85°F before they are shipped

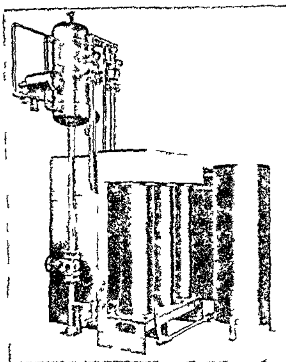
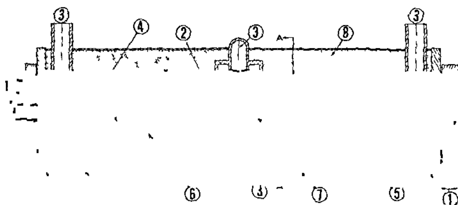
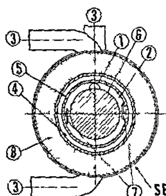


Fig 107 —Votator for shortenings or lard (Courtesy of *The Girdler Corp*)





(1) PRODUCT CONNECTIONS
(2) PRODUCT CHAMBER
(3) HEAT TRANSFER MEDIUM CONNECTIONS
(4) HEAT TRANSFER MEDIUM CHAMBER
(5) HEAT TRANSFER TUBE
(6) MUTATOR SHAFT
(7) SCRAPER BLADES
(8) INSULATION

Fig 108 —Votator cylinder, cross and longitudinal sections (Courtesy of *The Girdler Corp*)

(b) *Solidification of Margarine*

While methods for the solidification of margarine are in most respects similar to those employed for the solidification of shortening, certain complications are introduced by the circumstance that margarine is not a pure fat, but an emulsion consisting of about 80% plastic fat and 20% milk and salt.

Three different processes are used for solidifying this product. In these the emulsion of oil and aqueous liquid is respectively sprayed into cold water, solidified on the surface of a chilling roll, and solidified in a Votator. The three processes were developed in the order mentioned. At present the cold water method is very nearly obsolete, at least in the United States, whereas the roll method has to a considerable extent been supplanted by Votator solidification. As the two older methods are discussed in some detail in another chapter devoted to margarine manufacture in general, this section will be devoted to a further description of the Votator process.

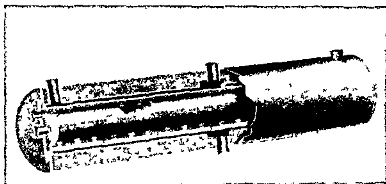


FIG. 109.—Votator cylinder, cut away view (Courtesy of *The Girdler Corp.*).

Obviously margarine could be handled in the Votator similarly to shortening, by simply beating the liquid fat and the milk, etc., into an emulsion, and then pumping this mixture through the machine. This was in fact the first method used, and is still the method preferred by some manufacturers, but it has certain disadvantages, hence at present special machines are employed for margarine manufacture, in which provision is made for handling the ingredients somewhat differently, if this is desired.

If all of the milk is fed with the oil to the Votator, the homogenizing action of the feed pump, scraper blades, etc. produces a much "tighter" emulsion than is ordinarily obtained in margarine, *i. e.*, the milk droplets are beaten into an abnormally fine state of subdivision. This is not wholly desirable for two reasons. It renders the aqueous phase quite invisible, so that the product loses the appearance of margarine and rather resembles shortening. Also it affects the flavor of the product adversely, since a very fine emulsion will taste less strongly of both salt and butterlike flavors

than the rather coarse emulsion usually encountered in margarine A further disadvantage to adding the milk with the oil feed is that by this method of operation all of the milk must necessarily be salted before it is incorporated with the fat The operation is entirely continuous, the Votator receives the various ingredients, solidifies and blends them, and discharges the margarine in the form of molded prints ready for wrapping, hence there is no opportunity for adding salt after solidification of the fat has taken place As explained in the chapter on margarine manufacture, salting of the milk effectively stops bacterial action, so that there is no opportunity for the development of butterlike flavors through the action of bacteria in contact with the fat

The scheme of operation adopted to avoid the above mentioned difficulties is illustrated in the flow diagram of Figure 110 A multicylinder reciprocating pump is used to deliver all ingredients under pressure to the Votator, this pump acting also as a proportioning device Approximately

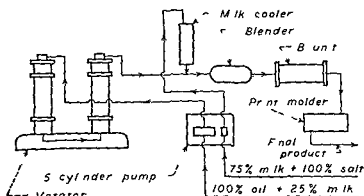


FIG 110 —Flow diagram, Votator system for solidification of margarine

25% of the milk and all of the oil is mixed together, and fed to the Votator in the usual way This mixture passes successively through two chilling chambers and then into a blender, which is similar to the "B" unit of the shortening Votator, and consists of a closed cylinder equipped with a mixer made up of a longitudinal shaft set with pins In the line leading from the chilling cylinders to the blender the solidified emulsion meets a stream of liquid consisting of the remaining 75% of the milk and all of the salt This milk is cooled to about 25°F in a special refrigerated precooler, and is mixed into the newly solidified material in the blender, without being dispersed there to any unusually high degree

This method of incorporating the milk produces in effect two intermixed dispersions of the aqueous phase One consists of a very finely dispersed system of unsalted milk, the other consists of a relatively coarse system of salted milk The fine emulsion of unsalted milk presents a sufficient interface to the fat for the adequate development of butterlike flavors, while the

coarse emulsion containing the bulk of the milk carries the salt flavor and gives the margarine the appearance and the slightly wet surface customarily found in margarines

From the blender the product is passed to a cylinder designated as the "B" unit, which contains a system of homogenizing screens, but no agitator In this unit the fat is allowed to set up sufficiently to be printed The "B" unit discharges into a hydraulically operated print molder, which forms it into one pound prints ready to be wrapped and packaged

The standard two cylinder machine has a rated capacity of 3000 pounds of margarine per hour Its total power and refrigeration requirements are respectively, 26 horsepower and 15 standard tons

(c) *Solidification of Soaps*

The commercial solidification of soaps is described in the chapter on soapmaking, hence it will be unnecessary to discuss the subject at any length here The previously described methods of solidifying plastic fats each have their counterpart in the processing of soap, and whereas continuous, closed systems, as exemplified by the Votator, have not assumed the importance in soapmaking that they have in the shortening and margarine industries, there nevertheless appears to be a trend in their direction The continuous solidification of soaps is closely allied with the subject of polymorphism in soap crystals Since the implications of polymorphism in soaps have only very recently been recognized, it is to be expected that continued research in soap processing may eventually yield continuous methods to replace completely the present somewhat tedious processes of flaking, drying, milling, plodding, etc

A continuous solidification process utilizing the Votator principle has recently been applied to the manufacture of lubricating greases These materials are plastic solids consisting of a liquid phase of mineral oil and a solid phase of soap fibers hence the principles applicable to the solidification of pure soaps likewise hold in their case This is true regardless of the fact that the soaps used in making greases are often soaps of calcium, aluminum, lithium, etc , rather than of sodium

3. Emulsification of Oils with Aqueous Liquids

The dispersion of one liquid in another, to form an emulsion,[2] is not very different in principle from the dispersion of a solid in a liquid As the liquid particles comprising the discontinuous phase become smaller in size they tend to behave more and more like solids, being circumscribed by surface tension forces which maintain them in a relatively rigid spherical

[2] For a detailed discussion of methods and machines for forming technical emulsions, see Assoc Leather Trades Chemists, *Emulsion Technology* Chemical Pub Co , New York, 1944

form, and strongly resist deforming stress tending to cause further subdivision Because of the strength of surface tension in droplets of small dimensions, and the impossibility of applying force to overcome surface tension without wasting considerable energy in merely shearing the continuous phase, the power requirements for producing very fine emulsions are considerable

The type of emulsifying machine most commonly employed consists of some arrangement of mixer blades partially immersed and revolving

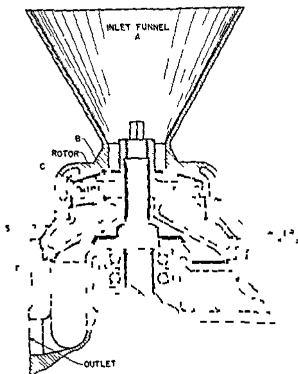


Fig 111 —Colloid mill (*A*) Inlet funnel, (*B*) impellers on top of rotor, (*C*) space between rotor and housing, site of first processing action (*D*) space between interlocking rings on bottom of rotor and top of stator, site of second processing action, (*E*) space between smooth sections of rotor and stator, site of third processing action, (*F*) chamber through which product discharges (Courtesy of *The C O Bartlett & Snow Co*)

rapidly in the liquids to be emulsified Often the operation is carried out in batches, and one of the liquids is slowly added to the batch while the latter is continually agitated In this form of emulsifier the kinetic energy of the blades striking the liquids is utilized to cause subdivision of one of the liquids and produce an emulsion Although this arrangement does not produce the finest emulsions, it is simple, relatively efficient from the standpoint of power consumption, and entirely satisfactory for many purposes A common example of emulsifier of this type is the ordinary

household egg beater Machines utilizing this principle are extensively used in commercial bakeries and mayonnaise plants They are in general best adapted to the discontinuous preparation of material in relatively small batches

Homogenizing valves are used to produce fine emulsions, as well as to break up aggregates of material in plastic fats These valves are in effect spring loaded constrictions or orifices They generate intense shearing forces in the liquid mixture as it is forced past them under high pressure These forces serve to break up the disperse phase more thoroughly than is possible in emulsifiers of the beater type The pumps used in connection with homogenizing valves are usually of the reciprocating type, and are built with a multiplicity of cylinders to deliver a steady flow of material to the valves They often produce pressure in excess of 1000 pounds per square inch Ordinarily a coarse emulsion is first produced by ordinary mixing of the two liquids, and the coarse emulsion is then further homo genized Homogenizing valves are particularly used for producing fine emulsions in ice cream mixes, condensed milk, fluid milk, and other dairy products Homogenization by this method is of course continuous

The finest emulsions are produced in so called colloid mills, which depend for their effect on the intense shear developed between accurately ground, fast revolving rotors, or rotors and stators operating with a clearance of the order of 0 001 inch, or less

A diagrammatic view of a typical colloid mill is shown in Figure 111 This particular mill employs a rotor and stator provided with concentric, interlocking rings, which impart a labyrinthine motion to particles of mate rial passing between the two and increase the area of the intervening film of material The rotor is further provided with vanes on its reverse surface which act as a centrifugal pump and force material through the mill from the periphery to the center of the rotor, against centrifugal force, thus maintaining the space between the rotor and stator in a flooded condition at all times, and consequently avoiding aeration of the emulsified product The rotor revolves at 10,800 r p m Water jackets are provided for cooling the stator Referring to the figure, the coarse emulsion fed to inlet funnel A is seized by impellers or vanes B on the top of the rotor, and forced successively through the constricted passages between rotor and stator indicated at C, D and E before it is discharged at F

Since the energy required for converting a coarse to a fine emulsion is measured more or less by the magnitude of the increase in the oil–water interface, the power required for carrying out emulsification in a colloid mill is quite high Thus for example, the mill described above requires a 7 5 horsepower motor for operating a 4 5 inch rotor, with a throughput of liquids of the order of 1–2 gallons per minute

Colloid mills are used for the processing of mayonnaise and for the preparation of very fine emulsions of a specialty nature

AUTHOR INDEX

A

B

C

D

N

SUBJECT INDEX